SURVEY OF FORMALDEHYDE IN THE INDOOR ENVIRONMENT

5.1   METHODS

In this section we describe the methods used to measure formaldehyde (HCHO) in the indoor environment, collect data on residence characteristics and other factors which may influence indoor formaldehyde concentrations, and analyze the collected data.

5.1.1   Lawrence Berkeley Laboratory Passive Sampler

Formaldehyde concentrations in residential and workplace air were measured with the Lawrence Berkeley Laboratory passive diffusion sampler. This device has a low sampling rate, which permits the evaluation of one-week, time-weighted average concentrations of formaldehyde at concentrations typically found in residences, from as low as 0.018 ppm to over 1 ppm. Though peak concentrations are not obtained, the sampler quickly responds to transient peaks and incorporates them into the time-weighted average (Hodgson et al., 1982). Table 5.1-1 describes the sampler and presents the results of laboratory and field validation experiments.

5.1.2   Indoor Formaldehyde Sample Site Selection

Eighty-one residences and 10 worksites were selected for indoor air formaldehyde measurement using passive diffusion samplers. (Six of these comprise a "supplementary sample" of new homes, which will be described in Section 5.2-6. The initial set of 75 residences will be referred to as the "original sample.") Of these, two were re-measured using an impinger sampling method, in order to identify aldehyde species present; impinger sampling results are presented in Section 5.2.7. Sites were selected in two steps: (1) definition of a sampling frame, and (2) random selection from the frame.

Table 5.1-1

DESCRIPTION AND SPECIFICATIONS OF THE LBL PASSIVE SAMPLER

CONTAMINANT:	Formaldehyde
SAMPLER:	Passive diffusion sampler; area, 3.98 cm^2; path length, 9.4 cm.
SAMPLING RATE:	4.02 cm^3/min (0.296 μg/ppm-hr) at 1 atm and 20^{0}C
SAMPLING PERIOD:	1 week (168 hr)
SAMPLING RANGE:	0.018 ppm to more than 1 ppm for 168 hr
ENVIRONMENTAL EFFECTS:	Independent of pressure, only slightly dependent on temperature (0.2%/1^{0}C)
	Accuracy reduced when average relative humidity exceeds 60% at 20^{0}C
INTERFERENCES:	No identified significant interferences in residential environments
SHELF LIFE:	2 weeks minimum
SAMPLE STABILITY:	2 weeks minimum
OVERALL PRECISION:	Mean coefficient of variation = 6.7%
BIAS:	+15% based on field comparisons with reference method; true concentration = 0.87 x passive sampler concentration
OVERALL ACCURACY:	True concentration $\pm$ 95% confidence interval of 14%

From Hodgson et al., 1982

Choice of Sampling Frame

The ideal sampling frame from which to select residences would be a list of all residences in the State of California, including names, addresses and phone numbers of occupants. Unfortunately, such a list does not exist. We considered using California property tax rolls as a sampling frame. These rolls list all properties for which property tax is paid in California, their addresses, and the names and addresses of their owners. Unfortunately, names of renters and their apartment numbers are not included, and no phone numbers are given. Since we wanted a cross section of housing types, we wanted to select a fair number of rented houses and apartments. If we had used property tax rolls we would have had to contact owners to obtain names of renters before asking the cooperation of the renters - a task we believe would have been difficult. Also, since we believe that phone contact is more efficient and more effective in obtaining participation than letter contact, we would have had to obtain phone numbers for all selected.

It was decided that the most practical sampling frame would be California telephone books, which include all residences with listed phone numbers. Names and phone numbers of both owners and renters are included, eliminating the need to contact owners to obtain names of renters. Unlike the case of property tax rolls, no additional step is required to obtain phone numbers. Pacific Telephone and Telegraph Company's Directory Library in Los Angeles includes most of the phone books for California. This collection of books was used as the sampling frame for the selection of potential residence sampling sites.

The difficulty of selecting a representative sample of worksites was discussed in the Interim Report (Ziskind et al., 1982). As recommended in the report and approved by the ARB, the workplace sample was constructed from the sample of residents.

Random Selection Process

Potential sampling sites were randomly selected by the following method.

(1) To insure selection of residences from a range of different climates and locations, potential sample sites were selected from five regions of California: North Coast, San Francisco Bay Area, Los Angeles-Long Beach, Sacramento Valley and San Joaquin Valley. According to the 1970 Census, 73 percent of all California residences are located in these regions.

(2) A list of phone books available in the Directory Library for each of the five regions was compiled.

(3) Within each region potential residence sample sites were randomly selected from available phone books by using a random number table in the following manner:

     o Randomly select phone book
     o Randomly select page in the phone book
     o Randomly select column on page
     o Randomly select residence

Name, address, phone number and random selection information were recorded on a "Formaldehyde Sample Site Selection Form" which was also used to record phone contact information and data on residence characteristics. This and all other survey forms are included in Appendix E. An attempt was made to contact each of the selected potential residence sample sites by telephone between 3 and 7 p.m. The telephone script used to obtain cooperation of residents is provided in Appendix E.

Table 5.1-2 is the "Sample Site Selection Screening Form." This form lists the housing characteristics we determined to be important for a survey of indoor formaldehyde. In the boxes, the left-hand numbers are the percentages of residences in the State of California with each particular characteristic, according to the 1970 census. Since we wanted our survey to be representative of the State of California, we wanted our sample to approximately follow these percentages. The right-hand number in each box is the number of residences with a particular characteristic we wanted to include in our original sample of 75 homes. As phone contact was made and participants were recruited, the residence characteristics were marked on this

Table 5.1-2

DESIRED DISTRIBUTIONS OF RESIDENTIAL
CHARACTERISTICS FOR INDOOR RESIDENTIAL FORMALDEHYDE SAMPLING SITES
(Sample Site Selection Screening Form)

	Single Unit	Other
I. Demographic Characteristics		
A. Owner Occupied [62% 50]		
1. Urban	[35% 28]	[19% 15]
2. Rural	[6% 5]	[2% 2]
B. Renter Occupied [38% 30]		
1. Urban	[23% 18]	[12% 10]
2. Rural	[3% 2]	[0% 0]
II. Location/Climate[a]		
A. North Coast	[2% 2]	
B. S.F. Bay Area	[22% 24]	
C. L.A. - Long Beach	[36% 40]	
D. Sacramento Valley	[5% 6]	
E. San Joaquin Valley	[8% 8]	
III. Age of Housing (years)		
33+	[24% 19]	
21-32	[13% 10]	
11-20	[30% 24]	
5-10	[14% 11]	
new-4	[14% 11]	
(5 should be new, energy-efficient)	[6% 5]	

4 blanks
6 residential duplicates
10 work site samples
75 residential site samples
5 resample

[a] Percentage do not add to 100 since all parts of the state were not included.

form and the sample distribution's characteristics were monitored. We were prepared to exclude potential participants if the distribution of residence characteristics did not approximate the desired distribution outlined in Table 5.1-2. Table 5.1-3 shows the distribution of characteristics of our original sample. Since not enough residences 0 to 4 years old were obtained, our supplementary sample selection was restricted to new housing.

5.1.3   Indoor Formaldehyde Sampling

We selected 81 residences for sampling and used 106 samplers. The first 10 participants who worked indoors and who were agreeable were requested to deploy an additional sampler at their workplace. Duplicate samplers were placed side-by-side in six residences. Five samplers were reserved for re-sampling, and four were used as field blanks. The field blanks were treated exactly the same as the non-blank samplers, except that they were uncapped, exposed to the indoor air for only a few seconds, and re-capped.

Participants were mailed passive formaldehyde samplers, a cover letter, a letter from the ARB authorizing the study, instructions for use of the sampler, a "Sample Site Data Sheet" requesting information about characteristics of the residence, a "Sampling Week Data Sheet" requesting information about events which occurred in the residence during the week the sample was taken and may have influenced formaldehyde exposure, and a stamped return envelope. All these forms are provided in Appendix E.

Participants were instructed to place the sampler in a room of their residence that the family frequently occupies. We suggested the room in which the television is located or the living room. Samplers were not to be placed in the kitchen, in or near a bathroom or near an open window. They were to be taped to a wall or door at "nose" level with the open end of the sampler pointing downward (to avoid collecting dust). Participants were instructed to uncap the sampler, tape it to a wall or door, record the date and time the sampler was uncapped, and fill out the "Sample Site Data Sheet." Figure 5.1-1 shows how the samplers were to be attached to the walls.

Table 5.1-3

OBTAINED DISTRIBUTIONS OF RESIDENTIAL CHARACTERISTICS FOR
INDOOR RESIDENTIAL FORMALDEHYDE SAMPLING SITES,
NON-MOBILE HOME RESIDENCES (ORIGINAL SAMPLE)

I. DEMOGRAPHIC CHARACTERISTICS	Single Unit	Other
A. Owner Occupied		
1. Urban	29	2
2. Rural	6	0
B. Renter Occupied		
1. Urban	9	18
2. Rural	0	0
	44	20

II. Location/Climate

A. North Coast	1
B. S.F. Bay Area	21
C. L.A. - Long Beach	31
D. Sacramento Valley	5
E. San Joaquin Valley	6

III. Age of Housing (years)

33+	19
21-32	13
11-20	19
5-10	12
new-4	1

  4 blanks
  6 residential duplicates
10 work site samples
64 residential site samples (non-mobile home)
  3 mobile homes
  3 lost/broken
  6 not returned
  4 resamples

100
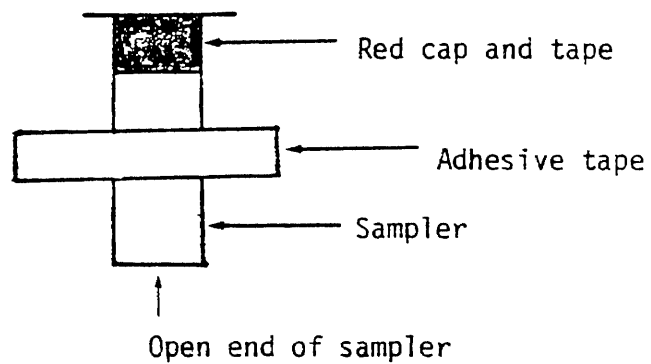
FRONT VIEW
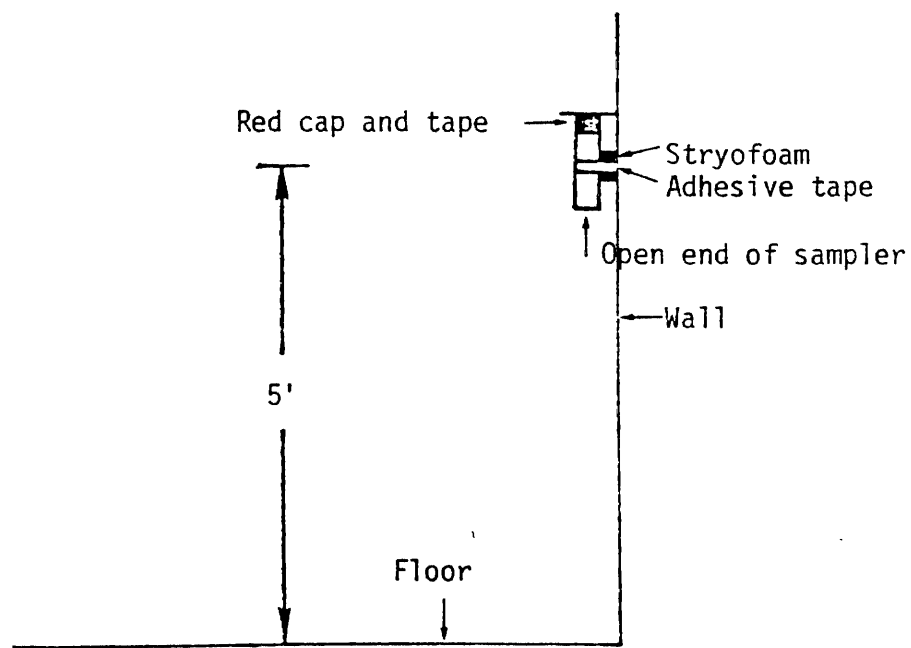
SIDE VIEW

Figure 5.1-1. Placement of Passive Formaldehyde Samplers.

A few days after the samplers were mailed, every participant was contacted by telephone. The purposes of this phone call were to verify that the sampler had been received in an undamaged condition; to answer any questions; and to verify that sampling had begun. If sampling had not been started the participant was asked to start sampling as soon as possible. If desired, verbal instructions for the use of the sampler were given over the phone. The date and time sampling had been started was requested and recorded on a master log sheet. Participants were told the appropriate date and time to re-cap the sampler and stop sampling.

Participants were instructed to deploy the sampler uncapped for one week, plus or minus one day. Sampling was terminated by re-capping the sampler and sealing the cap with tape. When sampling was terminated, participants were instructed to fill out the "Sampling Week Data Sheet." The sampler(s) and the two checklists were returned to SAI in the return envelope provided. A five dollar gift certificate to either Safeway Supermarket or McDonald's was mailed to each participant at the completion of sampling as a token gift.

5.1.4   Laboratory Analysis of Passive Formaldehyde Samplers

Samplers were sent to Lawrence Berkeley Laboratory (LBL) for chemical analysis. Analytical methods are described in detail in Appendix C. LBL's results were then provided to SAI for statistical analysis.

5.1.5   Statistical Analysis of Indoor Formaldehyde Data

The purposes of the statistical analysis were (1) to determine the relative importance of various factors in relationship to indoor formaldehyde concentrations and (2) to quantify formaldehyde exposures experienced by the general population. Data were collected on several potentially important indoor formaldehyde sources, various demographic characteristics, and other potentially important factors. The variables for which data were collected are listed in Table 5.1-4.

Table 5.1-4
LIST OF INDOOR FORMALDEHYDE VARIABLES

Variable	Codes	

RESIDENCE CHARACTERISTICS

Type of Residence	Single unit = 1	Other = 2
Owner vs. renter occupied	Owner occupied = 1	Renter occupied = 2
Urban vs. Rural	Urban = 1	Rural = 2
Geographic location	North Coast = 1	S.F. Bay Area = 2
	L.A./Long Beach = 3	Sacramento Valley = 4
	San Joaquin Valley = 5	
Age of Residence	New - 4 yrs = 1	5 - 10 yrs = 2
	11 - 20 yrs = 3	21 - 32 yrs = 4
	33+ = 5	
Type of Primary Heating Unit	Central = 1	Individual Room = 2
Heating Fuel	Gas = 1	Electric = 2
	Kerosene = 3	Other = 4
Cooking Fuel	Gas = 1	Electric = 2
	Other = 3	
Home Insulated	No = 0	Yes = 1
UF Foam	No = 0	Yes = 1
New Kitchen Cabinets	No = 0	Yes = 1
Recent Recarpeting	No = 0	Yes = 1
Energy Efficient Home	No = 0	Yes = 1
Number of Rooms	1 - 9 +	

EVENTS DURING SAMPLING

Heating Use	No = 0	Yes/Low = 1
	Yes/Med = 2	Yes/High = 3
Meals cooked	01 - 99 +	
Open windows	No = 0	Yes = 1
Fireplace Use	No = 0	Yes/Gas = 1
	Yes/Wood = 2	Yes/Other = 3
Cigarettes Smoked	No = 0	Yes/1 Pack or Less = 1
	Yes/>1, <5 packs = 2	Yes/5 + Packs = 3

FORMALDEHYDE CONCENTRATION   ppb

Several methods were used to determine which of the factors listed in Table 5.1-4 were the most important in affecting residential indoor formaldehyde concentrations. Results for mobile homes are discussed separately (see Section 5.2.3) since they differ from other residences in building materials and construction.

5.1.5.1 Determination of Factors Contributing to High HCHO Concentrations

First, an analysis was performed to explore the differences between residences with the highest and lowest formaldehyde concentrations. The residences with the 10 highest and 10 lowest formaldehyde concentrations were compared on various characteristics: type of dwelling, age of residence, type of heating fuel, type of cooking fuel, whether windows were open at any time during sampling, cigarette smoking during sampling, number of meals cooked during sampling, and whether the residence is "energy efficient" (i.e., cracks sealed to reduce air flow).

To test the association between each residence characteristic and high vs. low HCHO level, a Chi-square test of independence would generally be the statistical test of choice. However, when the counts in each cell are small (i.e., when more than 20 percent of the cells have counts less than 5) a Chi-square test is not valid and a Fisher's Exact Test should be used (Fleiss, 1981). Fisher's Exact Test was used here for this reason. A 2 x 2 table was constructed for each variable as shown below.

	Low HCHO	High HCHO	Total
Residence Characteristic 1	n_{11}	n_{12}	$n_{1.}$
Residence Characteristic 2	n_{21}	n_{22}	$n_{2.}$
Total	$n_{.1}$	$n_{.2}$	$n_{..}$

The exact significance level of the observed 2 x 2 table was obtained by evaluating the probability of obtaining the 2 x 2 table actually observed and the probabilities of obtaining all other possible 2 x 2 tables having the

same marginal frequencies ($n_{1.}$, $n_{2.}$, $n_{.1}$, $n_{.2}$), and adding the probability of the actually observed table with the probabilities of other tables less than or equal to the probability of the observed table (two-sided test).

The probability of observing each 2 x 2 table is calculated by the following formula:

$$p = \frac{n_{1.}!\ n_{2.}!\ n_{.1}!\ n_{.2}!}{n_{..}!\ n_{11}!\ n_{12}!\ n_{21}!\ n_{22}!}$$

The null hypothesis that was tested was that of no association between residence characteristics and HCHO level. A p-value less than 0.05 resulted in a rejection of the null hypothesis and the conclusion that an association exists between the tested residence characteristics and levels of HCHO in the indoor air in our sample of residences.

5.1.5.2 Analysis of Variance

Secondly, the effect on formaldehyde concentration of each of the variables listed in Table 5.1-4 for the entire sample of residences was examined. Using the Biomedical Computer Programs (BMDP), P-series, statistical package (Dixon, 1983), descriptive statistics were computed and histograms were drawn for subgroups, as well as for the entire sample. Side-by-side histograms were used to visually inspect the effect of a variable on formaldehyde concentrations. Subgroup means were statistically compared using a one-way analysis of variance test (ANOVA), program BMDP7D.

ANOVA is an overall test of whether differences exist among subgroup population means. It yields the probability of obtaining the observed results if each of the subgroups came from populations with equal means. For ANOVA to give valid results, the following assumptions must be met: (1) normally distributed data, (2) independent and random samples, and (3) equal population variances. Histograms were used to check the normality of the data. The samples are known to be independently random because of the manner in which they were chosen. Levene's Test for Equal Variances was used to test the equality of subgroup variances. When variances were found to not be similar, the Welch and Brown-Forsythe One-Way ANOVA tests were used; these tests do not require group variances to be equal.

5.1.5.3 Comparison of Homes Expected to Have Highest Versus Lowest HCHO

Third, mean HCHO concentrations were compared for homes expected to have the highest and lowest indoor concentrations. SAI determined from the published literature and the results of this survey that the variables potentially most important in affecting indoor HCHO concentrations were: type of cooking fuel, cigarette smoking, and whether windows were open during sampling. Homes with gas cooking fuel in which cigarettes were smoked were compared to homes with electric cooking in which cigarettes were not smoked. Also, homes with gas cooking, cigarettes smoked and closed windows were compared to those with electric cooking, no cigarettes smoked, and open windows. Group means were compared using a one-sided t-test.

5.1.5.4 Multiple Regression

Finally, a multiple regression analysis was performed to examine the joint relationship between all variables for which data were collected and indoor air HCHO concentration. The multiple regression equation is of the following form:

$$y' = a + b_1 x_1 + b_2 x_2 + \ldots + b_k x_k.$$

y' = the dependent variable, HCHO concentration
a = the intercept.
b = the regression coefficient for each independent variable.
x = an independent variable.

The multiple correlation coefficient, R^2, is a measure of the strength of the relationship between y (HCHO concentration) and $x_1, \ldots, x_k$ (the other variables included in the regression equation). R^2 can vary from 0 to 1; if R^2 is small the variables included in the regression equation do not explain very well the variation in the dependent variable, and there is little advantage in using $x_i, \ldots, x_k$ to predict y (Dunn and Clark, 1974). The multiple regression analysis was performed using programs BMDP2R (Stepwise Regression) and BMDP9R (All Possible Subsets Regression) in the BMDP statistical package (Dixon, 1983).

All variables used in a multiple regression must be placed along a single dimensional scale (Dunn and Clark, 1974). For this reason several of the variables listed in Table 5.1-4 were recoded. For example, the variable "Cooking Fuel" (gas=1, electric=2, other=3) was recoded as three separate variables, "gas cooking fuel" (0=no, 1-yes), "electric cooking fuel" (0=no, 1=yes) and "other cooking fuel" (0=no, 1=yes). The variables and codes used in the multiple regression analysis are listed in Table 5.1-5.

A major step in multiple regression analysis is the selection of independent variables to include in the regression equation. The multiple correlation coefficient, R^2, will be larger the greater the number of variables included in the equation (regardless of whether added variables really contribute to explaining the variation in the dependent variable). However, regression equations with large numbers of variables are generally less satisfactory in predicting the variation of the dependent variable than equations with smaller numbers of variables. Also, the regression coefficients for a given equation vary depending on which and how many variables are included in the equation.

In this analysis, regression equations were generated for many possible subsets of independent variables. The final regression equation was selected with the following objectives:

(1) Maximize R^2;
(2) Exclude those variables that result in very small increases in R^2.

5.2 RESULTS AND DISCUSSION

One hundred passive formaldehyde samplers were deployed: 4 field blanks, 10 work-place samples, 75 residence samples, 6 duplicate residence samples, and 5 samplers used for re-sampling. Two of the residential samples were lost during analysis at Lawrence Berkeley Laboratories, one was smashed in the mail from the residence to SAI, six were not returned to SAI, and 66 were sampled and analyzed. Two of the 66 residence samples were from mobile homes.

Table 5.1-5

LIST OF INDOOR HCHO VARIABLES:
MULTIPLE REGRESSION ANALYSIS

Variable	Codes		

Residence characteristics

Variable	Codes		
Single Unit	0=No		1=Yes
Apartment, Condo, etc.	0=No		1=Yes
Owner Occupied	0=No		1=Yes
Renter Occupied	0=No		1=Yes
S.F. Bay Area	0=No		1=Yes
L.A./Long Beach	0=No		1=Yes
Sacramento Valley	0=No		1=Yes
San Joaquin Valley	0=No		1=Yes
Age of Residence	1=New - 4 yrs	2=5-10	
	3=11-20	4=21-32	
		5=33+	
Central Heating	0=No		1=Yes
Individual Room Heating	0=No		1=Yes
Gas Heating Fuel	0=No		1=Yes
Electric Heating	0=No		1=Yes
Gas Cooking Fuel	0=No		1=Yes
Electric Cooking	0=No		1=Yes
Other Cooking Fuel	0=No		1=Yes
Home Insulated	0=No		1=Yes
Urea-formaldehyde Foam	0=No		1=Yes
New Kitchen Cabinets	0=No		1=Yes
Recent Recarpeting	0=No		1=Yes
Energy Efficient Home	0=No		1=Yes
Number of Rooms	1-9+		

EVENTS DURING SAMPLING

Variable	Codes		
Heating Use	0=No		1=Yes/Low
	2=Yes/Med		3=Yes/High
Meals Cooked	1-99		
Open Windows	0=No		1=Yes
Fireplace Use	0=No		1=Yes
Cigarettes Smoked	0=No		1=Yes/1 pack or less
	2=Yes/>1,<5 packs		
	3=Yes/5+ packs		

FORMALDEHYDE CONCENTRATION   ppb

The field blanks were determined to have 0.28, 0.43, 0.28, and 0.40 µg of HCHO, respectively, with a mean of 0.35 µg HCHO and standard deviation of 0.08.

Time-weighted average (TWA) formaldehyde concentrations in parts-per-billion (ppb) were calculated by subtracting the mean field blank HCHO weight from the HCHO weight for each sampler and applying the following formulas:

$$\frac{(\mu g\ HCHO)}{[(SR)\ (X)\ (60\ min/hr)]/1000} = \mu g\ HCHO/L$$

$$\frac{(\mu g\ HCHO/L)\ (MV)\ (1000)}{MW} = ppb\ HCHO$$

where

X = Sampling time in hours

MV = Molar volume at 25°C, 760 mm Hg = 24.47 L

MW = Molecular weight of HCHO = 30.03 g/mole

SR is the sampling rate of the passive sampler (4.02 cm^3/min), which was determined by exposing the samplers to known HCHO concentrations; it is a function of the diffusion coefficient of HCHO in air, the cross sectional area of the sampler and the diffusion path length (Hodgson et al., 1982).

As an example, sampler ID #2 was determined to have collected 4.43 µg HCHO during a sampling period of 205.5 hrs. The mean field blank HCHO weight of 0.35 µg was subtracted from this value, to obtain a corrected HCHO weight of 4.08 µg. A time-weighted indoor air HCHO concentration was then calculated as follows:

$$\frac{(4.08\ \mu g\ HCHO)}{[(4\ cm^3/min)(205.5\ hours)(60\ min/hr)]/1000} = 0.0827\ \mu g\ HCHO/L$$

$$\frac{(0.0827 \text{ µg HCHO/L})(24.47 \text{ L})(1000)}{30.03} = 67.41 \text{ ppb HCHO TWA}$$

5.2.1 Non-Mobile Home Residences

The mean formaldehyde concentration for the 64 non-mobile home residences was 49.8 ppb, with a standard deviation of 21.0. Concentrations ranged from 18 to 120 ppb. A frequency distribution of observed HCHO concentrations for non-mobile homes is presented in Table 5.2-1.

5.2.1.1 Determination of Factors Contributing to High HCHO Concentrations

In Table 5.2-2 the 10 residences with the highest TWA indoor air HCHO concentrations are compared to the 10 residences with the lowest HCHO levels for various residence characteristics. The probability of obtaining the observed distribution of HCHO levels by residence characteristics was tested with Fisher's Exact Test (two-sided), under the null hypothesis of no association between HCHO level and residence characteristics.

For example, of the 10 low HCHO homes 8 were single unit dwellings and 2 were other dwelling types; in comparison, 5 of the high HCHO homes were single unit dwellings and 5 were other dwelling types. A 2 x 2 table was constructed for the observed distribution of residences by residence type and HCHO level as shown for the example below:

	Low HCHO	High HCHO	Total
Single unit	8	5	13
Other	2	5	7
Total	10	10	20

The probability of obtaining the observed distribution of residences was calculated as follows:

$$p = \frac{13! \ 7! \ 10! \ 10!}{20! \ 8! \ 5! \ 2! 5!} = 0.15$$

Table 5.2-1

FREQUENCY DISTRIBUTION OF INDOOR AIR HCHO CONCENTRATIONS
FOR NON-MOBILE HOME RESIDENCES

HCHO Concentration	Frequency	Percent	Cumulative Percent
0-10 ppb	0	0.0	0.0
11-20	2	3.1	3.1
21-30	6	9.4	12.5
31-40	15	23.4	35.9
41-50	17	26.6	62.5
51-60	9	14.1	76.6
61-70	6	9.4	85.9
71-80	3	4.7	90.6
81-90	2	3.1	93.8
91-100	2	3.1	96.9
101-110	1	1.6	98.4
111-120	1	1.6	100.0
120+	0	0.0	100.0

Table 5.2-2

RESIDENCE CHARACTERISTICS COMPARED FOR HOMES WITH 10 HIGHEST
AND 10 LOWEST INDOOR HCHO CONCENTRATIONS

Residence Characteristic	Low[a] HCHO	High[b] HCHO	Exact Significance Level
RESIDENCE TYPE			
Single Unit	8	5	
Other	2	5	NS[c]
AGE OF HOUSING			
21+	5	5	
New-20	5	5	NS
PRIMARY HEATING FUEL			
Gas and Other	10	6	
Electricity	0	4	NS
PRIMARY COOKING FUEL			
Gas	4	6	
Electricity	6	4	NS
OPEN WINDOW			
No	5	4	
Yes	5	6	NS
CIGARETTES SMOKED			
No	9	4	
Yes	1	6	NS
ENERGY EFFICIENT HOME			
No	8	7	
Yes	2	3	NS
AVG. NO. MEALS COOKED	10.6	10.7	

[a] The 10 homes with the lowest HCHO concentrations had a mean HCHO concentration of 25.3 ppb.

[b] The 10 homes with the highest HCHO concentrations had a mean HCHO concentration of 87.3 ppb.

[c] Fisher's Exact Test (two-sided) was used to test the association between HCHO level and residence characteristics. NS means $p > 0.05$.

All other possible 2 x 2 tables with the same marginal values were also constructed, and their associated probabilities were computed (Figure 5.2-1). The exact significance level of Fisher's Exact Test was calculated by summing the probability associated with the actually observed 2 x 2 table and the probabilities of other possible 2 x 2 tables with equal or lesser probabilities. For example, the significance level associated with the variable "residence type" is equal to $0.15 + 0.15 + 0.027 + 0.027 + 0.0015 + 0.0015 = 0.357$. Since in this example p was greater than 0.05, the null hypothesis was not rejected and it was concluded that HCHO level and residence type may not be associated. The lowest p value for the variables tested, 0.057, was associated with cigarette smoking during sampling.

5.2.1.2 Analysis of Variance

Group mean time-weighted average indoor formaldehyde concentrations are presented in Table 5.2-3 for the entire sample with the results of Analysis of Variance (ANOVA) tests for equality of group means. Group means were found to be significantly different only for geographic location and type of heating fuel. Group means for residence age classes are discussed further in Section 5.2.6.

The relationship between number of meals cooked and HCHO concentration was further explored by separately examining meals cooked using gas vs. electricity. The comparison of group means and ANOVA are presented in Table 5.2-4. Results of similar analysis of gas versus electric heating use are also presented in Table 5.2-4. Sample ANOVA calculations are presented in Tables 5.2-5, 5.2-6, and 5.2-7, for the variable heating fuel.

The relationship between HCHO concentration and cigarette smoking was further explored. As noted above, the p value for a relationship between smoking and HCHO concentrations in the highest- and lowest-HCHO homes was not significant (Table 5.2-2, Fisher's Exact Test, $p = 0.057$, two-sided). Group means for different levels of smoking were not significantly different for the entire sample (Table 5.2-3, ANOVA, $p = 0.19$). However, we performed a final

Observed 2 x 2 Table   Low HCHO   High HCHO   Total

	Low HCHO	High HCHO	Total
Single unit	8	5	13
Other	2	5	7
Total	10	10	20

$p = 0.15$

Other Possible 2 x 2 Tables

	Low	High	
S.U.	9	4	
O.	1	6	$p = 0.027$

	Low	High	
S.U.	4	9	
O.	6	1	$p = 0.027$

	Low	High	
S.U.	10	3	
O.	0	7	$p = 0.0015$

	Low	High	
S.U.	3	10	
O.	7	0	$p = 0.0015$

	Low	High	
S.U.	7	6	
O.	3	4	$p = 0.33$

	Low	High	
S.U.	6	7	
O.	4	3	$p = 0.33$

	Low	High	
S.U.	5	8	
O.	5	2	$p = 0.15$

Exact Significance Level $= 0.15 + 0.15 + 0.027 + 0.027 + 0.0015 + 0.0015$
$$= 0.357$$

Figure 5.2-1. Sample Calculation of Fisher's Exact Test for the Variable "Residence Type."

Table 5.2-3
OOR FORMALDEHYDE CONCENTRATION
COMPARISONS OF GROUP MEANS AND ANOVA
FOR NON-MOBILE HOME RESIDENCES

Variable	Subgroup	N	Mean Formaldehyde Concentration (ppb)	Standard Deviation
TOTAL		64	49.8	20.9
RESIDENCE TYPE				
	Single unit	44	47.4	19.9
	Other	20	55.1	22.7
OWNER/RENTER OCCUPIED				
	Owner	37	48.7	19.7
	Renter	27	51.4	22.8
URBAN/RURAL				
	Urban	58	50.1	21.3
	Rural	6	46.9	18.5
GEOGRAPHIC LOCATION[a]				
	North Coast	1	23.0	0.0
	S.F. Bay Area	21	54.8	27.5
	L.A./Long Beach	31	49.7	17.6
	Sacramento Valley	5	50.9	13.8
	San Joaquin Valley	6	36.6	5.8
AGE OF RESIDENCE				
	New-4 yrs	1	65.0	0.0
	5-10 yrs	12	46.4	13.9
	11-20 yrs	19	48.9	22.4
	21-32 yrs	13	55.8	15.5
	33+ yrs	19	48.1	26.6
TYPE OF PRIMARY HEATING UNIT				
	Central	46	49.6	21.0
	Individual Room	18	50.5	21.5

[a] Group means significantly different at 0.05 level as determined by One-Way Analysis of Variance.

Table 5.2-3
(continued)

Variable	Subgroup	N	Mean Formaldehyde Concentration (ppb)	Standard Deviation
HEATING FUEL[a]				
	Gas	50	47.4	18.1
	Electric	11	65.1	28.0
	Kerosene	0	0.0	0.0
	Other	3	34.3	10.0
COOKING FUEL				
	Gas	34	52.9	21.9
	Electric	30	46.4	19.6
	Other	0	0.0	0.0
HOME INSULATED				
	No	26	47.3	15.4
	Yes	38	51.6	24.1
UF FOAM				
	No	60	49.9	21.4
	Yes	4	49.3	13.6
NEW KITCHEN CABINETS				
	No	59	49.3	21.5
	Yes	5	56.0	13.3
RECENT RECARPETING				
	No	53	50.4	21.1
	Yes	11	47.3	20.8
ENERGY EFFICIENT HOME				
	No	51	49.6	21.5
	Yes	13	50.7	19.3
NUMBER OF ROOMS				
	2	3	40.6	14.2
	3	4	52.8	11.6
	4	17	61.5	26.3
	5	13	48.5	20.1
	6	5	45.3	13.9
	7	8	40.0	11.7
	8	8	46.3	20.4
	9+	6	44.0	22.0

[a] Group means significantly different at 0.05 level as determined by One-Way Analysis of Variance.

Table 5.2-3
(continued)

Variable	Subgroup	N	Mean Formaldehyde Concentration (ppb)	Standard Deviation
HEATING USE				
	No	3	38.3	7.5
	Low	24	53.1	17.2
	Medium	33	49.4	24.8
	High	4	42.1	8.7
MEALS COOKED				
	5 or less	13	58.8	24.0
	6 to 10	18	39.9	17.2
	11 to 15	22	54.4	21.7
	over 15	10	47.6	16.0
	missing data	1	24.0	0.0
OPEN WINDOWS				
	No	29	48.6	21.7
	Yes	35	50.9	20.6
FIREPLACE USE				
	No	47	52.5	22.4
	Yes/Gas	3	51.0	15.7
	Yes/Wood	13	42.2	13.3
	Yes/Other	1	21.0	0.0
CIGARETTES SMOKED DURING SAMPLING WEEK				
	No	38	46.1	19.0
	1 Pack or Less	14	56.9	26.4
	More than 1, less than 5	4	42.9	11.8
	5+	8	58.8	19.9

Table 5.2-4

INDOOR FORMALDEHYDE CONCENTRATIONS: COMPARISON OF GROUP MEANS AND ANOVA FOR GAS VS. ELECTRIC COOKING AND HEATING DURING SAMPLING PERIOD[a]

Variable	Subgroup	N	Mean HCHO Conc. (ppb)	Std. Dev.
MEALS COOKED (GAS)				
	5 or less	9	56.1	24.2
	6 to 10	9	44.3	20.6
	11 to 15	13	59.2	22.5
	Over 15	3	41.7	3.5
MEALS COOKED (ELECTRICITY)				
	5 or less	4	64.8	26.0
	6 to 10	9	35.6	12.6
	11-15	9	47.4	19.4
	Over 15	7	50.1	18.9
	Missing Data	1	34.0	0.0
HEATING USE (GAS)				
	No	1	31.0	0.0
	Low	19	49.7	14.6
	Med	28	46.9	20.7
	High	2	40.5	10.6
HEATING USE (ELECTRICITY)[b]				
	No	2	42.0	5.6
	Low	5	66.2	21.6
	Med	2	107.0	18.4
	High	2	43.8	10.3

[a] Non-mobile home residences only.

[b] Group means significantly different at 0.05 level as determined by one-way ANOVA tests.

Table 5.2-5

SAMPLE ANOVA CALCULATION:
INDOOR HCHO CONCENTRATIONS (ppb) FOR
HOMES WITH DIFFERENT TYPES OF HEATING FUEL

Gas					Electricity	Other
32 ppb	43	48	40	50	100 ppb	38
67	35	33	31	79	41	42
45	58	48	50		38	23
56	37	55	50		46	
68	26	51	34		57	
73	54	58	33		120	
34	32	103	63.5		94	
47	61	78	37		68	
46	47	81	34		65	
31	45	22	27		51	
82	57	18	43		36.5	
21	42	22	42			

	Gas	Electricity	Other
n_i	50	11	3
$\sum_{j=1}^{n} Y_{ij}$	2,369.5	716.5	103
$\bar{Y}_{i\cdot}$	47.39 ppb	65.14 ppb	34.33 ppb
$\bar{Y}_{\cdot\cdot}$	49.83 ppb		

$\sum_{j=1}^{n} Y_{ij}$ = Sum of observations for each group

$\bar{Y}_{i\cdot}$ = Group mean HCHO concentration

$\bar{Y}_{\cdot\cdot}$ = Overall mean HCHO concentration

Table 5.2-6

ANALYSIS OF VARIANCE TABLE FOR ONE-WAY CLASSIFICATION,
MODEL I, UNEQUAL NUMBERS: EQUATIONS

Source of Variation	Sum of Squares	d f	Mean Square	Computed F
Due Treatment	$SS_a = \sum\limits_{i=1}^{a} n_i (\overline{Y}_{i.} - \overline{Y}_{..})^2$	$a-1$	$MS_a = SS_a/(a-1)$	MS_a/s_e^2
Residual	$SS_r = \sum\limits_{i=1}^{a} \sum\limits_{j=1}^{n_i} (Y_{ij} - \overline{Y}_{i.})^2$	$N-a$	$s_e^2 = SS_r/(N-a)$	

a = no. of treatments

N = total no. of observations

n_i = no. of observations in a group

$\overline{Y}_{i.}$ = Group mean HCHO concentration

$\overline{Y}_{..}$ = Overall mean HCHO concentration

Y_{ij} = The "jth" observation for the "ith" group

Table 5.2-7

ANALYSIS OF VARIANCE TABLE FOR ONE-WAY
CLASSIFICATION, MODEL I, UNEQUAL NUMBERS:
RESULTS OF CALCULATIONS FOR THE VARIABLE HEATING FUEL

Source of Variation	Sum of Squares	df	Mean Square	F Value	P Value[a]
Between Groups	3595.25	2	1797.63	4.56	0.014
Within Groups	24052.36	61	394.30		

[a] Obtained by comparing F value to F distribution table.

comparison for the entire sample: HCHO concentrations in homes where cigarettes were smoked (N = 26, mean = 55.3 ppb, s = 22.8) versus homes where cigarettes were not smoked (N = 38, mean = 46.1 ppb, s = 19.0). Mean HCHO concentrations were found to be significantly higher in homes where cigarettes were smoked, using a one-sided t-test (t = 1.75, df = 62, p < 0.05). Thus, cigarette smoking does appear to be associated with increased indoor air formaldehyde in our sample of residences. The difference between mean HCHO concentrations for homes where cigarettes were smoked versus homes where they were not smoked was 9.2 ppb.

Mean HCHO concentrations were significantly different for homes in different geographic areas (Table 5.2-3, ANOVA, p = 0.05). Highest to lowest mean HCHO concentrations were found in the San Francisco Bay Area, Sacramento Valley, Los Angeles/Long Beach, and San Joaquin Valley, respectively. The one North Coast home was excluded from the ANOVA test because a sample of 1 results in a variance of 0. San Francisco Bay Area, Los Angeles/Long Beach, and Sacramento Valley homes had relatively similar mean HCHO values. The distribution of HCHO values for the San Joaquin Valley homes was different from those for homes in the other geographic areas, with all 6 values being low and close together; this difference in distribution of HCHO concentrations is most likely responsible for the statistical significance of this ANOVA test.

The characteristics of the six San Joaquin Valley homes were examined to determine why their distribution of HCHO concentrations was so different. All had more than 5 rooms, central heating, and no new kitchen cabinets; 5 had gas heat, electric cooking, and insulation; were single unit dwellings, owner occupied, located in an urban area, less than 20 years old, not energy efficient; and had at least 10 meals cooked during the week of sampling. They were not similar for any of the other variables for which data were collected. It is not immediately apparent why these 6 homes had lower and more tightly grouped HCHO concentrations than homes in other geographic locations. However, the small sample size (N = 6) increases the potential for spurious correlations; the correlation of low HCHO values and the San Joaquin Valley homes sample may not reflect the real situation in the population from which the sample was taken.

For all sampled homes, mean HCHO concentrations for subgroups with different types of heating fuel were significantly different (Table 5.2-3, ANOVA, p = 0.014). However, the observed results are contrary to what might be expected: high HCHO concentrations were associated with electric heating. The high mean value for the 11 electric heating homes was due to 3 homes with very high HCHO concentrations: 120, 100 and 94 ppb. When these 3 outliers (which are more than two standard deviations from the mean of all samples) are excluded, the mean HCHO level for the remaining 8 electric heating homes is 50.3 ppb, just slightly higher than the mean value for gas heating homes. Two of the three high-HCHO homes fell into the category of medium use of electric heating (Table 5.2-4) and are largely responsible for the significant results seen in that analysis. In addition, no dose-response relationship was observed between mean HCHO concentration and level of use of gas heating, electric heating or for all heating methods combined. It is doubtful that either heating method or number of meals cooked is truly associated with differing HCHO levels in our sample of California residences.

5.2.1.3 Comparison of Homes Expected to Have Highest Versus Lowest HCHO

Based on the published literature it was expected that the factors in our data set most likely to affect indoor HCHO concentrations would be type of cooking fuel, cigarette smoking, and whether windows are opened during sampling. Homes with gas cooking fuel in which cigarettes were smoked during sampling (N = 12, mean HCHO = 63 ppb, s = 26) were compared with homes with electric cooking and no cigarette smoking (N = 16, mean HCHO = 44, s = 21). Using a one sided t-test, the 19 ppb difference in HCHO concentration between these two groups of homes was statistically significant (t = 2.12, df = 26, p < 0.025, one-sided). To consider a third factor, homes with gas cooking fuel, cigarette smoking, and closed windows (N = 6, mean HCHO = 67, s = 30) were compared to homes with electric cooking, no cigarettes smoked, and windows open some time during sampling (N = 7, mean HCHO = 53, s = 25). Using a one-sided t-test, the difference between these group means was not statistically significant (t = 1.04, df = 15, p < 0.20, one-sided).

A multiple regression analysis was performed using the variables listed in Table 5.1-5. The variables included in the "best" regression equation were the following: insulated home (0 = no, 1 = yes), number of rooms (1-9+), cigarette smoking during sampling (0 = no, 1 = yes/low, 2 = yes/medium, 3 = yes/high), individual room heating (0 = no, 1 = yes), gas heating fuel (0 = no, 1 = yes), gas cooking fuel (0 = no, 1 = yes), and fireplace use during sampling (0 = no, 1 = yes). These variables, their corresponding coefficients and t statistics, and R^2 are listed in Table 5.2-8. In addition, a matrix showing the correlation between each of the variables is presented in Table 5.2-9.

The R^2 for this equation is low. Therefore we must conclude that most of the variation in HCHO concentration is not explained by these variables. None of the other variables for which data were collected were found to add much to the explanatory power of this equation. It is likely that HCHO variation also depends to a large extent on factors for which data were not collected in this study, such as air exchange rates.

5.2.2   Repeat Sampling of Residences

Five of the 100 samplers were reserved for resampling. The outcomes of the first and second sampling periods for these 5 residences are compared in Table 5.2-10. At the ARB's request, one sampler was deployed in a mobile home that had not been included in the first sampling period. The results of this sampling are discussed in Section 5.2.3.

Samplers from three homes included in the first period were not analyzed because of post-sampling mishaps. The repeat sampling results for these homes are discussed separately from those obtained during the first period because (1) sampling occurred during a different month and results may not be comparable due to different climatic conditions; and (2) all three repeat samplers yielded very low HCHO concentrations, two of which were the lowest for all passive diffusion samplers deployed in this study. The characteristics of these three residences are listed in Table 5.2-11.

Table 5.2-8

INDOOR AIR HCHO:
SUMMARY OF MULTIPLE REGRESSION ANALYSIS

Variable	Coefficient	T-Statistic
Insulated Home	9.21	1.58
No. of Rooms	-2.30	-1.44
Cigarette Smoking	2.67	1.12
Individual Room Heating	- 7.62	-1.21
Gas Heating Fuel	-16.03	-2.10
Gas Cooking Fuel	13.39	2.42
Use of Fireplace	-9.72	-1.73
Intercept	65.32	
R^2	0.254	

Table 5.2-9

INDOOR AIR HCHO:
CORRELATION MATRIX FOR
MULTIPLE REGRESSION ANALYSIS

	Insulation	Rooms	Cigarette Smoking	Individual Room Heating	Gas Heating	Gas Cooking	Fireplace Use
Insulation	1.000						
Rooms	0.474	1.000					
Cigarette Smoking	-0.010	-0.132	1.000				
Individual Room Heating	-0.261	-0.405	0.002	1.000			
Gas Heating	-0.053	0.340	-0.216	-0.342	1.000		
Gas Cooking	-0.139	-0.009	-0.134	0.100	0.412	1.000	
Fireplace Use	0.137	0.157	-0.007	-0.061	-0.110	-0.144	1.000
HCHO Conc.	0.100	-0.208	0.187	0.020	-0.222	0.157	-0.213

Table 5.2-10

COMPARISON OF INDOOR FORMALDEHYDE
CONCENTRATIONS FOR FIRST AND SECOND
SAMPLING PERIODS

First Sampling Period	Second Sampling Period
Mobile Home, Not Sampled	68 ppb
79 ppb	37
Broken in mail	26
Spilled during analysis	$<18^a$
Broken in mail	$<18^a$

[a] Below the detection limit of 18 ppb.

Table 5.2-11

INDOOR FORMALDEHYDE CONCENTRATIONS:
COMPARISON OF CHARACTERISTICS FOR 3
RESAMPLED RESIDENCES[a]

Variable	Subgroup	N
TOTAL		3
RESIDENCE TYPE		
	Single unit	3
	Other	0
OWNER/RENTER OCCUPIED		
	Owner	2
	Renter	1
URBAN/RURAL		
	Urban	3
	Rural	0
GEOGRAPHIC LOCATION		
	North Coast	0
	S.F. Bay Area	0
	L.A./Long Beach	2
	Sacramento Valley	0
	San Joaquin Valley	1
AGE OF RESIDENCE		
	New-4 yrs	0
	5-10 yrs	0
	11-20 yrs	1
	21-32 yrs	1
	33+ yrs	1
TYPE OF PRIMARY HEATING UNIT		
	Central	3
	Individual Room	0

[a] These 3 homes had HCHO concentrations of 26, <18 and <18 ppb.

Table 5.2-11
(continued)

Variable	Subgroup	N
HEATING FUEL		
	Gas	3
	Electric	0
	Kerosene	0
	Other	0
COOKING FUEL		
	Gas	3
	Electric	0
	Other	0
HOME INSULATED		
	No	1
	Yes	2
UF FOAM		
	No	3
	Yes	0
NEW KITCHEN CABINETS		
	No	2
	Yes	1
RECENT RECARPETING		
	No	2
	Yes	1
ENERGY EFFICIENT HOME		
	No	3
	Yes	0
NUMBER OF ROOMS		
	2	0
	3	0
	4	1
	5	0
	6	0
	7	1
	8	0
	9+	1

Table 5.2-11
(continued)

Variable	Subgroup	N
HEATING USE		
	No	1
	Low	1
	Medium	1
	High	0
MEALS COOKED		
	55 or less	0
	6 to 10	2
	11 to 15	1
	over 15	0
OPEN WINDOWS		
	No	0
	Yes	3
FIREPLACE USE		
	No	3
	Yes/Gas	0
	Yes/Wood	0
	Yes/Other	0
CIGARETTES SMOKED DURING SAMPLING WEEK		
	No	0
	1 pack or less	2
	More than 1, less than 5	0
	5+	1

Indoor HCHO concentrations of 79 and 37 ppb were obtained for one residence during the original and follow-up sampling periods, respectively. Conditions during both periods were identical: moderate use of heating, 6 meals cooked, windows were open at some time during sampling, no use of a fireplace, no smoking of cigarettes, and the sampler was placed in the family room.

5.2.3 Mobile Homes

Two mobile homes were originally sampled, and one of the five samplers reserved for re-sampling was deployed in a third mobile home, at the request of the ARB. The three mobile homes had time-weighted average (TWA) indoor formaldehyde concentrations of 144, 130 and 68 ppb, with a mean of 114 and standard deviation of 40.4. In comparison, the non-mobile home residence concentrations ranged from 18 ppb to 120 ppb with a mean of 49.8 ppb. The distribution of the three mobile homes by residence characteristics is presented in Table 5.2-12.

According to Mr. Ken Hallmark of the California State Department of Housing and Community Development (personal communication) some newer mobile homes are being constructed with ceiling exhaust vents to reduce indoor air pollution levels. The owner of the mobile home with the lowest HCHO concentration was telephoned and asked if his home was constructed with such a vent. It was not. Thus, this is not the reason for the large difference in HCHO concentrations between his mobile home and the other two.

5.2.4 HCHO in Workplace Air

Ten participants deployed samplers both in their residences and at their workplaces. Time-weighted average indoor air HCHO concentrations are listed in Table 5.2-13 for the workplaces and residences of the 10 participants. One participant returned only his workplace sampler, despite repeated telephone calls. The high HCHO concentration (98 ppb) for this participant's workplace is suspect since the participant did not record the sampling start and end times and could not reliably recall them.

Table 5.2-12

INDOOR FORMALDEHYDE CONCENTRATIONS:
MOBILE HOMES

Variable	Subgroup	N	Mean Formaldehyde Concentration (ppb)
RESIDENCE TYPE			
	Single unit	3	114
	Other	0	0
OWNER/RENTER OCCUPIED			
	Owner	2	99
	Renter	1	130
URBAN/RURAL			
	Urban	2	106
	Rural	1	130
GEOGRAPHIC LOCATION			
	North Coast	0	0
	S.F. Bay Area	1	144
	L.A./Long Beach	1	68
	Sacramento Valley	0	0
	San Joaquin Valley	1	130
AGE OF RESIDENCE			
	New-4 yrs	1	68
	5-10 yrs	1	144
	11-20 yrs	1	130
	21-32 yrs	0	0
	33+ yrs	0	0
TYPE OF PRIMARY HEATING UNIT			
	Central	3	114
	Individual Room	0	0

Table 5.2-12
(continued)

Variable	Subgroup	N	Mean Formaldehyde Concentration (ppb)
HEATING FUEL			
	Gas	3	114
	Electric	0	0
	Kerosene	0	0
	Other	0	0
COOKING FUEL			
	Gas	3	114
	Electric	0	0
	Other	0	0
HOME INSULATED			
	No	2	137
	Yes	1	68
UF FOAM			
	No	3	114
	Yes	0	0
NEW KITCHEN CABINETS			
	No	3	114
	Yes	0	0
RECENT RECARPETING			
	No	3	114
	Yes	0	0
ENERGY EFFICIENT HOME			
	No	3	114
	Yes	0	0
NUMBER OF ROOMS			
	2	1	68
	3	0	0
	4	0	0
	5	0	0
	6	2	137
	7	0	0
	8	0	0
	9+	0	0

Table 5.2-12
(continued)

Variable	Subgroup	N	Mean Formaldehyde Concentration (ppb)
HEATING			
	No	0	0
	Low	0	0
	Medium	3	114
	High	0	0
MEALS COOKED			
	5 or less	1	130
	6 to 10	1	144
	11 to 15	1	68
	over 15	0	0
	missing data	0	0
OPEN WINDOWS			
	No	1	130
	Yes	2	99
FIREPLACE USE			
	No	3	114
	Yes/Gas	0	0
	Yes/Wood	0	0
	Yes/Other	0	0
CIGARETTES SMOKED DURING SAMPLING WEEK			
	No	2	137
	1 Pack or Less	0	0
	More than 1, less than 5	0	0
	5+	1	68

Table 5.2-13

COMPARISON OF INDOOR FORMALDEHYDE
CONCENTRATIONS FOR WORKPLACES AND RESIDENCES
(All Concentrations in ppb)

Workplace	Residence
38	65
14	67[b]
98[a]	-
23	46
23	21
36	43
41	51
30	94
40	27
57	22
Mean = 33.6 ppb[c]	Mean = 48.4

[a] This value is suspect due to participant's inaccurate recollection of start and end dates/times of sampling.

[b] Residence sampler not returned.

[c] Probably inaccurate value of 98 ppb excluded from calculation of mean value.

Indoor air HCHO concentrations for workplaces had a mean value of 33.6 ppb. This is lower than the mean for the residences of the participants who deployed the workplace samples (48.4 ppb) and for all non-mobile home residences combined (49.8 ppb). The characteristics of the workplaces are presented in Table 5.2-14. Because of the small number of workplace samples and the small number of variables for which data was collected, no clear conclusions can be drawn regarding HCHO in the workplace and workplace characteristics.

5.2.5   Duplicate Samples

In six residences, two samplers were placed side-by-side as a test of sampler reliability. For one of the pairs, only one sampler was returned to SAI. The remaining 5 pairs of samplers were found to have measured the following HCHO concentrations (in ppb): 32 and 33, 36 and 30, 64 and 63, 39 and 34, 20 and 26.

5.2.6   Supplementary Sampling Results

Passive samplers were returned by six of the nine new residences to which they were sent. Table 5.2-15 describes these residences and presents the results of the laboratory analysis of the samples. Formaldehyde concentrations ranged from 46 to 153 ppb, and had a mean and standard deviation of 84.5 and 37.5 ppb, respectively. In order to determine whether the mean concentration measured in "new" residences (0 to 4 years old) was significantly different from that measured in the older residences in the survey, the one new house which had been included in the original sample was added to the supplementary sample. The mean and standard deviation for this combined new residence group were 81.7 and 35.0 ppb, respectively. Using a two-sided t test, it was then determined that the mean for the new houses was significantly higher than for the houses in all other age groups ($p < 0.05$). Given the small sampling size, no attempt was made to discern relationships between formaldehyde concentrations and the characteristics of the supplementary sample.

Table 5.2-14

CHARACTERISTICS OF SAMPLED WORKPLACES[a]

Type of Building	Able to Open windows?	Carpet?	Underground Parking?	HCHO Conc. (ppb)
Highrise Office	No	Yes	Yes	57
School	Yes	Yes	No	41
Office	Yes	Yes	No	40
ARB Office	No	Yes	No	38
4-story office	No	Yes	No	36
1-story office	No	Yes	No	30
2-story office	Yes	Yes	No	23
3-story office	Yes	Yes	No	23
Office	No	No	No	14

[a] Information on workplace characteristics not available for workplace with 98 ppb HCHO.

Table 5.2-15

MEASURED FORMALDEHYDE CONCENTRATIONS AND STRUCTURAL AND ACTIVITY VARIABLES ASSOCIATED WITH RESIDENCES IN THE SUPPLEMENTARY SAMPLE
(Codes are defined in Table 5.1-4)

Variable	Residence Sample Number					
	NHS 2	NHS 3	NHS 4	NHS 6	NHS 7	NHS 9
RESIDENCE CHARACTERISTICS						
Type of Residence	1	2	1	2	1	2
Owner vs. Renter Occupied	1	2	2	2	1	2
Urban vs. Rural	1	1	1	1	1	1
Geographic Location	3	3	3	3	3	3
Age of Residence	1	1	1	1	1	1
Type of Primary Heating Unit	4^a	1	1	1	1	1
Heating Fuel	4^a	1	1	2	1	1
Cooking Fuel	1	1	1	1	1	2
Home Insulated	1	1	1	1^b	0	1
UF Foam	0	0	0	1^b	0	0
New Kitchen Cabinets	0	0	0	0	0	0
Recent Recarpeting	0	0	1	0	0	0
Energy Efficient Home	1	1	0	1^b	0	1
Number of Rooms	7	5	7	4	7	5
EVENTS DURING SAMPLING						
Heating Use	0	0	1	1	1	0
Meals Cooked	8	1	7	14	4	5
Open Windows	0	1	1	1	1	1
Fireplace Use	0	0	0	0	0	0
Cigarettes Smoked	0	0	0	0	1	0
Sampling Dates (June 1983)	6-13	1-8	4-11	2-9	3-10	3-10
FORMALDEHYDE CONCENTRATION	46	81	153	58	93	76

[a] Wood-burning heaters used.

[b] Respondent uncertain.

5.2.7   Species Composition of Indoor Carbonyls

In order to obtain an idea of the distribution of carbonyl species in indoor air, one-hour impinger sampling was conducted at two of the homes in the original passive monitoring group. (Impinger sampling methods are described in Section 6.2.) Results are presented in Table 5.2-16. Formaldehyde constituted 61 and 80 percent by volume of the total carbonyls present in the two houses. In both houses, acetaldehyde was the next most common species. Results from these tests cannot be directly compared with the passive monitoring results for these houses since (1) they represent one-hour, rather than weekly, averages, and (2) they were not conducted concurrently.

5.2.8   Summary and Conclusions

Indoor air HCHO concentrations appeared to be much higher for mobile homes than for other residence types. However, since only three mobile homes were sampled in this study, this observation remains to be confirmed by other indoor air HCHO surveys. Indoor air HCHO levels were generally higher for residences than for workplaces.

For non-mobile home residences, higher group mean HCHO concentrations were significantly associated with cigarette smoking (yes versus no) during the week of sampling. The mean HCHO concentration in homes in which cigarettes were smoked was 9 ppb higher than the mean concentration in homes where cigarettes were not smoked. Homes with gas cooking fuel in which cigarettes were smoked were found to have a significantly higher mean indoor HCHO concentration than homes with electric cooking and no cigarette smoking, by an average of 19 ppb.

The significant association between HCHO concentration and cigarette smoking may not mean that cigarettes smoking is the most important source of indoor formaldehyde. Participants were instructed to place the sampler in a room where the family spends a significant amount of time (other than the kitchen and bathroom), which is also the room in which smoking is likely to occur. In contrast, other potential sources of formaldehyde may be located in other rooms of the house (for example, the stove is in the kitchen). Thus,

Table 5.2-16

ONE-HOUR CONCENTRATIONS OF CARBONYL SPECIES IN
TWO CALIFORNIA RESIDENCES

Species	Residence 1 (ppb)	Residence 2 (ppb)
Formaldehyde	19.2	30.0
Acetaldehyde	7.1	2.6
Acetone	2.2	1.0
Acrolein	ND[a]	0.1[b]
Propanal	ND	ND
Methyl Ethyl Ketone	2.0	1.3
Butanal	ND	ND
Benzaldehyde	ND	0.6
Hexanal	1.0	2.1
Total Carbonyl	31.5	37.7

[a] ND = Below lower detection limits for acrolein (0.4 ppb), propanal (0.13 ppb), butanal (0.16 ppb) or benzaldehyde (0.04 ppb).

[b] This value is below the lower detection limit and may not be valid.

other potentially important HCHO sources may not have been as strongly associated with indoor HCHO concentration because they were located at a farther distance from the sampler.

Our original sample of 64 non-mobile home residences had TWA air HCHO concentrations ranging from 18 to 120 ppb (Table 5.2-1), with a mean of 49.8 ppb and standard deviation of 21.0. A supplementary sample of six new non-mobile homes had HCHO concentrations ranging from 46 to 153 ppb and a mean and standard deviation of 84.5 and 37.5 ppb, respectively. We expect indoor air HCHO concentrations in California homes to follow this same distribution pattern. In addition, our data suggest that homes in which cigarettes are smoked will have higher indoor air HCHO concentrations than homes in which cigarettes are not smoked, by an average of approximately 9 ppb. Homes in which cigarettes are smoked and gas cooking fuel is used are likely to have higher indoor HCHO concentrations than homes with no cigarette smoking and electric cooking, by an average of 19 ppb.

5.3   REFERENCES

Dixon, W.J. (Ed.). 1983. BMDP statistical software, 1983 printing with additions. University of California Press, Berkeley, CA.

Dunn, O.J. and V.A. Clark. 1974. Applied statistics: analysis of variance and regression. John Wiley and Sons, New York, NY.

Fleiss, J.L. 1981. Statistical methods for rates and proportions, 2nd Edition. John Wiley and Sons, New York, NY.

Hodgson, A.T., K.L. Geisling, B. Remijn, and J.R. Girman. 1982. Validation of a passive sampler for determining formaldehyde in residential indoor air. Lawrence Berkeley Laboratory, University of California, LBL-14626, UC-95d.

Ziskind, R.A., M.B. Rogozen, D. Grosjean, A.E. Shochet, A.F. Hadermann and R.E. Snokes. 1982. Formaldehyde: a survey of airborne concentrations and sources, Interim report. Prepared by Science Applications, Inc. for California Air Resources Board, SAI-068-83-033.

"HOT SPOT" EXPOSURE SAMPLING

6.1   SELECTION OF SOURCES AND SITES

The purpose of this portion of the field investigation was to determine whether formaldehyde concentrations were significantly higher than normal background levels in the vicinity of purported major point emission sources. Since source testing and modeling were beyond the scope of this project, our approach was to measure upwind and downwind concentrations associated with each source type. As reported in Chapter 2, airports, power plants, refineries, and urea-formaldehyde and phenol-formaldehyde resin plants were suspected of being important point sources. One facility of each type was therefore selected for field sampling. In addition, we decided to perform measurements in an enclosed shopping mall, since outgassing of formaldehyde from certain types of new clothing could result in elevated exposures to shoppers.

6.1.1   Rationale for Selection

Specific sources were selected for the following reasons.

Airport. Los Angeles International Airport was chosen because it is the largest facility of its type in the state and because access to sampling sites was relatively convenient.

Refinery. A major problem with assessing exposures due to refinery operations was that all the major refineries are in heavily industrialized areas, in which other formaldehyde sources may be present. The Chevron refinery in El Segundo was originally chosen because of its isolation, but suitable meaurement sites were unavailable. We chose to perform the tests around Mobil Oil Corporation's Torrance refinery since the terrain was relatively flat (affording line-of-sight view of major sources within the facility), convenient sampling sites were available, and nearby residential areas are downwind of the plant at least some of the time.

Power Plant. Again, we wished to perform tests at a relatively isolated facility, to minimize confounding factors. Southern California Edison's Ormond Beach Generating Station was considered ideal, since it is surrounded by flat, open farmland. Its location on the coast guaranteed very low background levels of formaldehyde during times of onshore air flow, thus obviating the need for upwind sampling.

Resin Plant. Our survey of California resin manufactures (see Section 2.2.1) indicated that the Borden Chemical and Reichhold Chemicals, Inc. plants in Fremont and South San Francisco, respectively, were large formaldehyde users. The Reichhold facility was chosen because access to suitable sampling sites was more convenient.

Shopping Mall. Requests for permission to sample were made to several Southern California shopping malls. The only one to give us permission stipulated that its identify be confidential. The mall is large and heavily used, and contains many clothing stores.

6.1.2   Choice of Measurement Sites

The presence of other formaldehyde sources (motor vehicles in particular) makes it difficult to isolate the contribution of the "hot spot" sources to ambient formaldehyde concentrations. Since most of the sites were in urban areas, it was impossible to avoid interference from automobile traffic. We minimized this interference, wherever possible, by

- Sampling upwind of major streets and highways;
- Using low buildings and other objects to shield the sampling site from the immediate effects of motor vehicle exhaust; and
- Sampling at times of light traffic (e.g. on a Sunday).

Another problem was that, with the exception of the power plant case, we did not have a good idea before the sampling where maximum concentrations were likely to occur. Such pre-estimates would have required extensive modeling, which was beyond the scope of the project. Even if we had been able

to pinpoint optimum sampling locations, two problems would still have remained. First, wind directions shifted frequently; very few of our one-hour measurements were made under constant wind speed and direction. In addition, to judge from our experience with modeling emissions from the power plant, the "optimum" sampling points would likely have been downwind from freeways or other confounding formaldehyde sources. A solution to those problems, which was not possible in this project, would have been to deploy samplers in several downwind sectors during each sampling hour. As a compromise, we decided to make the measurements in residential areas where possible, so that public exposures (be they the maximum likely exposures or not) could be assessed. For sources in heavily industrialized areas, we chose sites within 2 km of the facility.

6.2 SAMPLING AND ANALYTICAL METHODS

6.2.1 Field Sampling Methods

Samples were collected by drawing air through 30-ml midget impingers (Kontes Glass Company) containing 10 ml each of DNPH reagent (prepared by dissolving 2.5 g of 2,4-dinitrophenylhydrazine in 1 L of 2N hydrochloric acid) and an organic solvent (a 10:1 by volume mixture of cyclohexane and isooctane). MSA Model G portable vacuum pumps, whose batteries were recharged the night before each test day, were used. Immediately before and after each sample collection, air flow rates were measured with a rotameter (Dwyer Instruments, Inc., Michigan City, IN). Although our intention was to sample one liter per minute, this was not possible for some of the early tests, since a defective charger had left some of the portable pumps with insufficient power. Rotameters were calibrated with a Hewlett-Packard Model 0101-0113 soap film flowmeter. Calibration curves are shown in Appendix A.

Our sampling protocol consisted of the following steps:

(1) Set up a ring stand
(2) Measure flow rate with a rotameter.
(3) Transfer reagent and organic solutions from storage vials to the impinger.
(4) Connect the impinger to the pump and collect a one-hour sample.
(5) Disconnect the impinger, pour its contents into the original reagent vial, and rinse the impinger twice with 10 ml of distilled, deionized water.

(6) Measure the flow rate with a rotameter.

Wind speed and direction were measured at some of the sites with a Climatronics portable field weather station. At all the sites ambient air temperatures were measured with a 110°C immersion thermometer (VWR Scientific, Inc., Part No. 466177). Reagent and solvent mixtures and exposed samples were stored on blue ice in styrofoam chests at all times. To preclude introduction of particulate matter into the sample, impinger inlets were fitted with 5-cm Teflon tubes containing a wad of glass wool. To minimize any untoward effects of solar radiation, the impinger was wrapped in aluminum foil during sampling and, where necessary, was shaded with a garment or a towel.

Immediately upon return from the field, samples were stored in a refrigerator along with unused reagent and solvent solutions. They were then delivered to ERT in three batches. To assure that ERT laboratory personnel analyzed the samples "blind," each sample was labeled with a code number whose meaning was known only by SAI. ERT laboratory protocols are described in Appendix B. Results of analysis of quality assurance samples are presented in Appendix D.

6.2.2 Data Reduction

ERT provided SAI with the mass of formaldehyde detected in each sample. The air volume sampled in the field, V_f, was calculated by multiplying the average flow rate for each run by the sampling time. Since V_f was generally measured at a different temperature than that present in the room during rotameter calibration (24°C), it was necessary to adjust the volume by the following formula:

$$V_a = V_f \left[(t_c + 273)/(t_f + 273) \right]^{1/2} \qquad (6.2\text{-}1)$$

where t_c and t_f are the calibration and field temperatures ($^\circ$C), respectively, and V_a is the adjusted sample volume.

The ideal gas law is used to calculate the ratio between volumes of pollutant and volumes of air from the mass detected (W):

$$C_V = \frac{W(\mu g) \; 10^{-6} \; (g/\mu g) \; (0.08205 \; L\text{-}atm/mole\text{-}{}^{\circ}K) \; (t_f + 273.15)}{V_a(m^3) \; 10^3 \; (L/m^3) \; M(g/mole) \; (1 \; atm)} \qquad (6.2\text{-}2)$$

where M is the molecular weight. Since t_c was $24{}^{\circ}C$ in our case, V_a is equal to $V_f(17.2383)(273.16 + t_f)^{-1/2}$. Substituting this into Equation 6.2-2, we obtain:

$$C_V = \frac{4.7598 \times 10^{-12} \; W \; (t_f + 273.15)^{1.5}}{V_f M} \qquad (6.2\text{-}3)$$

To convert to parts per billion (ppb) by volume, we multiply by 10^9:

$$C_V \; (ppb) = \frac{4.7598 \times 10^{-3} \; W(t_f + 273.15)^{1.5}}{V_f M} \qquad (6.2\text{-}4)$$

Finally, we substitute the molecular weight of formaldehyde, 30.0, for M:

$$C_V \; (ppb) = \frac{1.5867 \times 10^{-4} \; W \; (t_f + 273.15)^{1.5}}{V_f} \qquad (6.2\text{-}5)$$

Sample calculations are presented in Appendix A. To calculate the volumetric concentrations of the species detected in the HPLC analysis, we used the corresponding molecular weights: acetaldehyde (44.1), acetone (58.08), acrolein (56.1), propionaldehyde (58.1), methyl ethyl ketone (72.1), butanal (72.1), benzaldehyde (106.1) and hexanal (100.16).

To estimate the total likely concentration when front and backup impingers both collected detectable amounts of formaldehyde, we used the method of Smith (1979). Let Y be the ratio of the first impinger concentration to the sum of the concentrations detected by the two impingers. The overall efficiency of the sampler train, e, is then:

$$e = 2/Y - 1/Y^2 \qquad (6.2\text{-}2)$$

The likely concentration is then estimated by dividing the measured concentration by e.

6.3   SITE-SPECIFIC METHODS AND RESULTS
6.3.1   Los Angeles International Airport

"Hot spot" sampling was conducted around Los Angeles International Airport (LAX) on 9 January 1983.

6.3.1.1 Sampling Sites

Figure 6.3-1 shows the sampling sites, while Table 6.3-1 reports the sampling schedule. Site 1-A (Aviation Boulevard) was on the Atchison, Topeka and Santa Fe Railroad right-of-way, about 100 m north of the intersection of Aviation Boulevard and 111th Street. From the air sampling site, one had a clear view down the southernmost runway, which departing planes used for taxiing to the next runway to the north. Wind speed, direction and temperature measurements were made at a wall about 100 ft (30 m) south of the impinger sampling point.

Site 1-B was Vista del Mar Park, which is on the east side of Vista del Mar Boulevard, which runs along the coast. The park is on a hillside. A chain-link fence marking the eastern boundary of the park is about 2,100 feet (640 m) from the extreme western end of the northern set of runways, although intervening dunes prevent a view of the airport. Wind measurements and sample collection were performed at the fence, at the highest point in the park.

Site 1-C was a small traffic island just east of the intersection of Arbor Vitae Street, Will Rogers Street and Kittyhawk Avenue. The site is slightly north of the eastern extension of the northern runways and is directly north of the eastern end of the southern runways. From it, one could see the main terminal builidings. Local automobile traffic was negligible. The flight path for planes landing on the northern runways was a_ t 1400 ft (430 m) south of the sampling site.
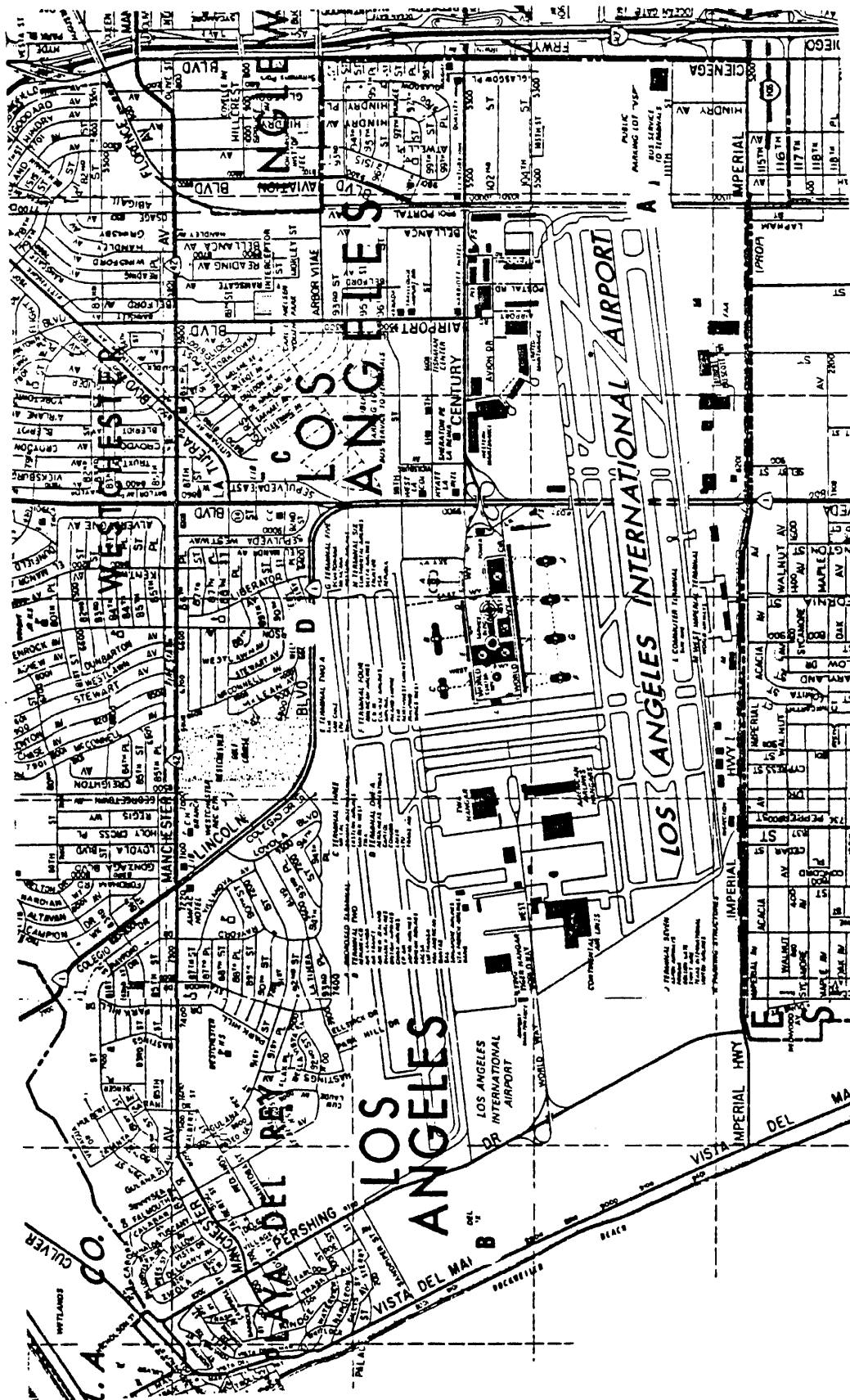
Figure 6.3-1. Sampling Sites Around Los Angeles International Airport.

Table 6.3-1

FORMALDEHYDE SAMPLING SCHEDULE AT LOS ANGELES INTERNATIONAL AIRPORT

Site No. [a]	Location	Sampling Times (hours of day)	Upwind/ Downwind	Sample Numbers	Comment
1-A	Aviation Blvd. near 111th St.	1000 1000-1100 1500-1600	- Upwind Downwind	1-5 1-8 1-3, 1-7	Field blank Parallel samples
1-B	Vista del Mar Park	1000-1100 1500-1600	Downwind Upwind	1-6 1-1	
1-C	Arbor Vitae and Kittyhawk	1705-1805	Downwind	1-4	
1-D	Will Rogers and Emerson	1705-1805	Downwind	1-2	

[a] Shown in Figures 6.3-1 and 6.3-2 as A, B, C, and D.

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Site 1-D was on a vacant lot near the intersection of Will Rogers Street and Emerson Avenue. The site is north of the eastern end of the northern runways. Since it was on a small cliff above Lincoln Boulevard, and traffic was light, effects of auto exhaust were believed to be minimal.

6.3.1.2 Sampling Conditions

Wind speed and directon and temperature readings were made in the morning at Site 1-A and in the afternoon at Site 1-B. In the morning the wind was steadily from the east, so that Sites 1-A and 1-B were upwind and downwind, respectively. Between 1500 and 1600 hrs the wind was steadily from the southwest, so that Site 1-B was clearly upwind and Site 1-A was downwind, but perhaps considerably off the centerline of the "plume" of emissions from the airport. Sites 1-C and 1-D were chosen to take advantage of the southwest wind. At 1700 hrs the wind was still from the southwest. About halfway through the last sampling period, it appeared to shift at Site 1-D to a northeast or northern wind. (The weather station was not used.) At Site 1-C, on the other hand, it appeared to be a southwest wind for the entire hour. Throughout the day, winds were calm (<2 m/sec) except at Site 1-B, where they rose to about 5 m/s between 1530 and 1600 hrs.

During both the morning and afternoon sampling, both of the airport's sets of runways were used for takeoffs and landings. From 1000 until 1025 hrs all takeoffs and landings were toward the west; for the rest of the hour they were towards the east. In the afternoon they were once again towards the west. Airport activities visible from Site 1-A during the morning were as follows:

	To West	To East	Total
Takeoffs (jet)	8	27	35
Takeoffs (propeller)	0	4	4
Landings (jet)	10	16	26
Landings (propeller)	4	0	4
Trucks on access road			22

In addition, three jets taxied to within 100 m of the sampling site. In the afternoon, we observed 20 landings and 117 takeoffs at the southern set of runways. (The morning figures are for both sets of runways, although not all of the northern runway activity was visible.)

6.3.1.3 Special Sampling Provisions

Before any sampling took place, a field blank (Sample No. 1-5) was created by mixing reagent and solvent in an impinger and immediately pouring the liquid back into the reagent vial. As an additional quality assurance measure, parallel samples (1-3 and 1-7) were collected at Site 1-A.

6.3.1.4 Results and Discussion

Results of the sampling and analysis are presented in Table 6.3-2. Concentrations ranged from 6.0 to 28.6 ppb, all of which values are within the normal range for ambient air in Los Angeles in January. Before discussing these results it is necessary to address two quality assurance issues. First, the field blank contained 0.49 µg of formaldehyde. Since the impinger in which the field blank was collected had not yet been used in any field work and had been extensively cleaned beforehand, it is unreasonable to attribute the high collection value to contamination. It is the opinion of ERT (Wright, 1983) that the 0.49 µg value is an artifact of the laboratory analysis, and should be considered to be anomalous. It was therefore not subtracted from the raw mass. The other issue is the 13-percent variation from the mean concentration of the simultaneously collected samples (1-3 and 1-7). Differences of 5 to 10 percent are typically obtained at HCHO levels of 15 to 20 ppb. (See Appendix D.) Contamination during field handling was possible.

Figure 6.3-2 shows an outline of the airport, along with measured concentrations (in ppb) at the sampling sites, which are indicated by dots. Arrows show the average wind direction during the sampling. During the second afternoon sampling period, the weather station was not used, so the wind angle cannot be known with accuracy; however, both sampling sites were downwind from the airport runways for most of the interval. No major effect of airport operations on ambient formaldehyde concentrations can be discerned from our

Table 6.3-2

RESULTS OF ANALYSES OF LOS ANGELES INTERNATIONAL AIRPORT SAMPLES

Sample Number	Mass [a] (μg)	Volume (m³)	Temperature (°C)	Raw[b] Concentration (μg/m³)	Adjusted[b] Concentration (ppb)	Comments
1-1	0.89	0.0687	21.5	12.95	10.4	
1-2	0.70	0.0651	18.5	10.75	8.5	
1-3	1.40	0.0573	21.5	24.43	19.6	
1-4	2.25	0.0624	19.2	36.06	28.6	
1-5	0.49	-	-	-	-	Field blank. See text
1-6	0.47	0.0639	26.0	7.36	6.0	2-3 drops exposed reagent lost.
1-7	1.28	0.0678	21.5	18.88	15.1	
1-8	1.09	0.0594	25.0	18.35	15.0	

[a] Provided by ERT.

[b] Raw concentration = mass/volume; adjusted concentration calculated after correcting for temperature. (See Section 6.2.2.)

6.0

B

15.0

A

1000 - 1100

10.4

B

15.9

A

1500 - 1600

8.5   28.6

D   C

1705 - 1805
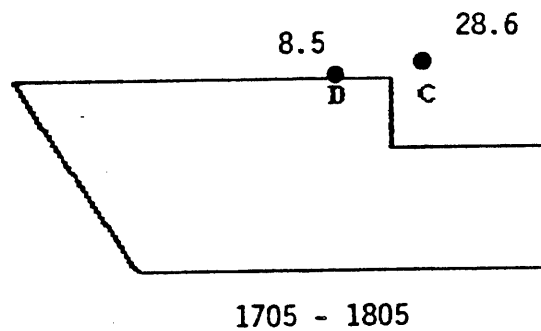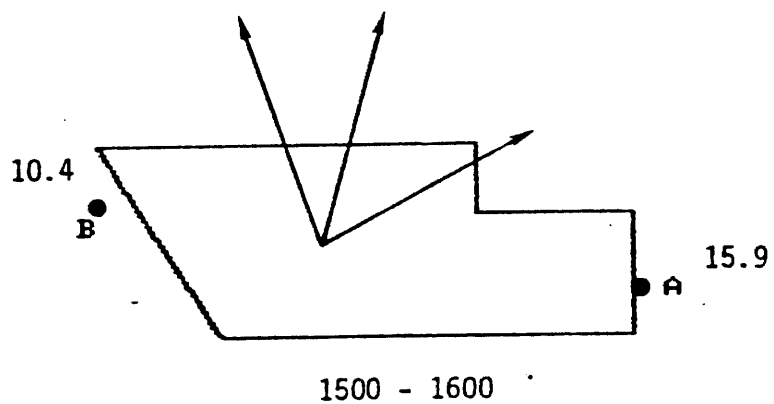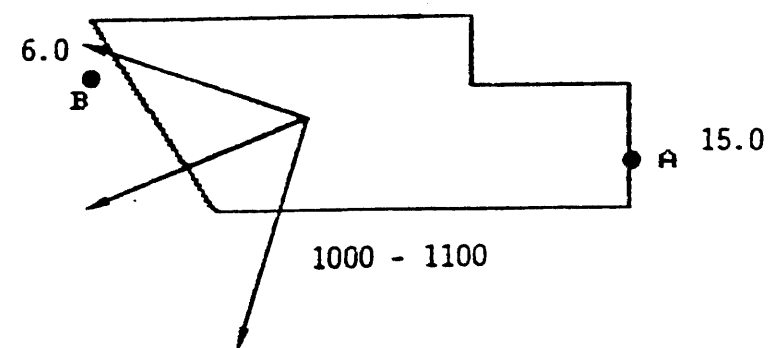
Figure 6.3-2. Formaldehyde Concentrations (ppb) Measured Around Los Angeles
International Airport. Arrows Indicate Range and Mean of
Wind Directions During Sampling.

results. In the morning, upwind concentrations were higher than those at the downwind site. The higher upwind concentrations may have been due to vehicular emissions from the San Diego Freeway (I-405), about 1 km due east. Given the wind direction during 1500-1600 hrs, neither site appears to be clearly upwind or downwind. (Note that until 20 minutes before this sampling interval, the wind was directly from the west, so that the Aviation Boulevard site would have been decidedly downwind. However, the wind shifted while a technician was en route to the downwind site. By then it was too late to change sites. In the late afternoon, the highest concentration of the day was measured at Site 1-C. The odor of jet fuel and exhaust was particularly strong at this location. At the same time, the second lowest concentration of the day was observed at the other ostensibly downwind site.

6.3.2   Mobil Oil Refinery, Torrance

Tests were conducted between 1000 and 1710 hrs on 11 January 1983 around Mobil Oil Corporation's Torrance refinery.

6.3.2.1   Sampling Sites

Figure 6.3-3 shows the sampling sites, while Table 6.3-3 reports the sampling schedule. Site 2-A was on the north shoulder of Del Amo boulevard near where Del Amo makes a sharp east-to-south turn and becomes Maple Avenue. The site is approximately 500 ft (150 m) southwest of the southwest corner of the refinery, and is situated on a short mesa adjacent to a horse stable approximately 30 ft (9 m) above the ground level of the refinery. The area is primarily light industrial and commercial. Vehicle traffic was fairly light, averaging 9 vehicles per minute. The weather station pole was placed in a special hook-up attached to a parked vehicle at the site, while the inlet impinger was placed about 3.5 ft (1 m) above the ground.

Site 2-B was on the northwest corner of the intersection of Erminita Avenue and 187th Place. The area is primarily residential, although a plant nursery is located on Erminita, on either side of 187th. Erminita Avenue at this intersection is quite narrow, so that the effects of traffic on heavily-
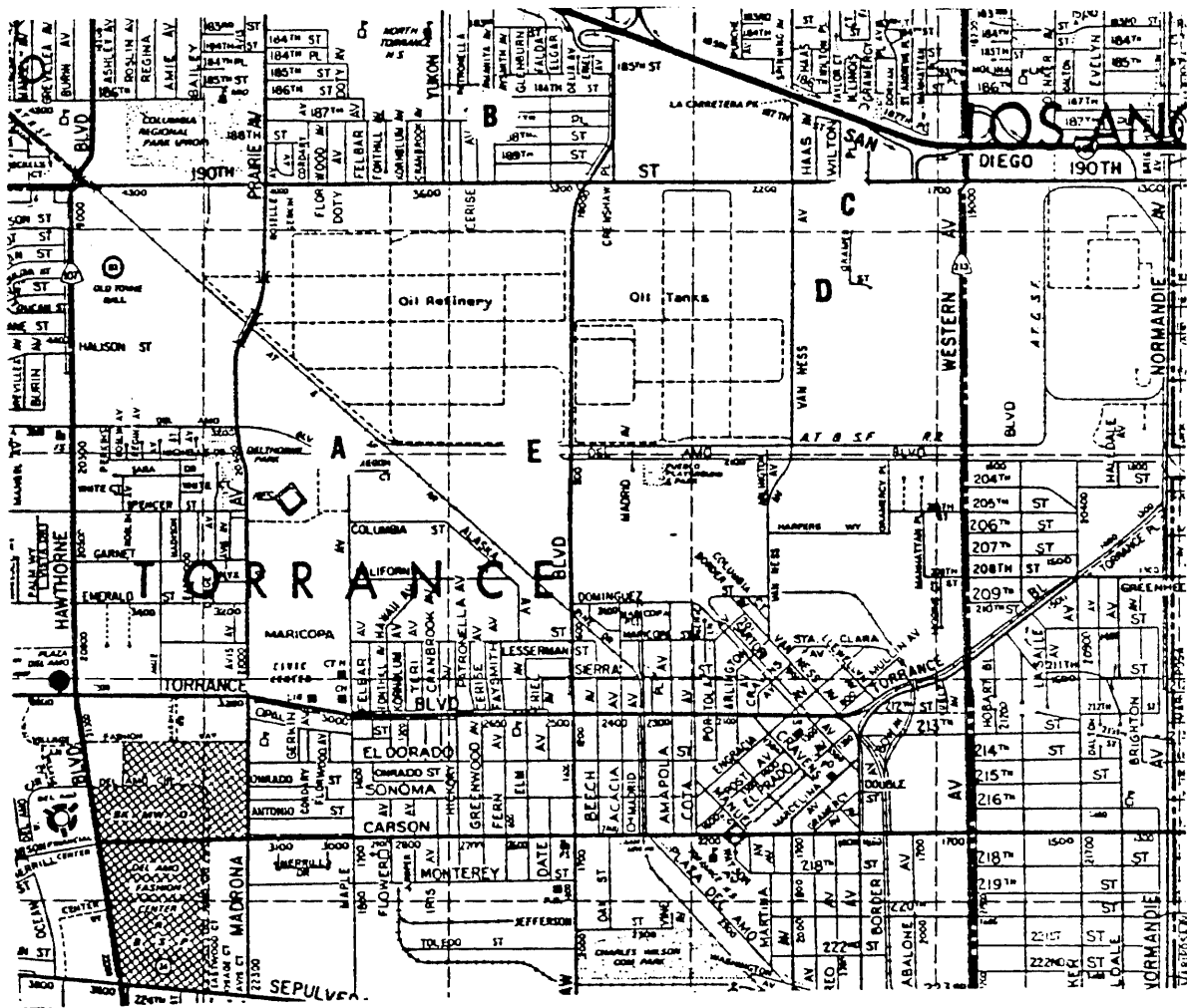
Figure 6.3-3. Sampling Sites Around the Mobil Oil Corporation Refinery in Torrance.

Table 6.3-3

FORMALDEHYDE SAMPLING SCHEDULE AT REFINERY

Site No.[a]	Location	Sampling Times (hours of day)	Upwind/ Downwind	Sample Numbers	Comments
1-A	Del Amo Blvd. and Maple	1000-1100	Upwind	2-2	
2-B	Erminita and 187th	1000-1100	Downwind	2-7 2-1	Front impinger Backup impinger
2-C	190th and Gramercy	1315-1514	Downwind	2-5	
2-D	196th near Gramercy	1315-1415 1610-1710	Downwind Downwind	2-4 2-6	
2-E	Del Amo Blvd. and Crenshaw	1610-1710	Downwind	2-3	

[a] Shown in Figure 6.3-3 as A, B, C, D, and E.

6-15

travelled 190th Street (three blocks to the south) would be minimal. From the sampling point, the refinery was clearly visible. The impinger inlet was placed about 5 ft (1.6 m) above the sidewalk. Local automobile traffic was negligible.

Site 2-C was located in the center of an empty lot measuring approximately 400 ft by 375 ft (120 m by 110 m) on the southwest corner of 190th Street and Gramercy Place. The area is primarily commercial on the north side of heavily used 190th Street, and light industrial.and commercial in all other directions. Traffic on Gramercy Place was negligible. The refinery was not visible from the site because of the surrounding structures. Site 2-C was located approximately 1,100 ft (335 m) north of Site 2-D (see below). The impinger inlet was placed about 3.5 ft (1 m) above the ground.

Site 2-D was on the south side of 195th Street, about 360 ft (110 m) east of Van Ness Avenue. On the west side of Van Ness were storage tanks and a gas flare about 40 ft (13 m) above the ground. A large cooling tower was visible to the west-northwest. Across the street from the sampling site were one-story industrial buildings and parking lots. To the south was a large empty field. The weather station pole was set up at a barbed wire fence demarcating this field, while the impinger inlet was placed about 4.5 ft (1.5 m) above the ground.

Site 2-E was located on Del Amo Boulevard, 600 ft (183 m) west of Crenshaw Boulevard. The site was 30 ft (9 m) south of the southern fence of the refinery. This part of Del Amo Boulevard is a very narrow road which dead ends about 700 ft (210 m) west of Crenshaw Boulevard. To the south are several moderately-sized storage tanks belonging to a chemical company. To the north, the site had an unobstructed view of the main refinery. Several stacks were visible to the north and northwest, the closest being about 400 ft (122 m) away. Residential and industrial areas are located east of the site while railroad right-of-way runs towards the west. The impinger inlet was placed atop a vehicle, about 8 ft (2 m) off the ground.

6.3.2.2 Sampling Conditions

The day was clear, sunny and hot. (The temperature was a record high for this date.) Wind speeds were generally below 5 m/s and were virtually nil at times. In the morning the wind was initially from the south, so that Sites 2-A and 2-B were to be upwind and downwind, respectively. According to the weather station readings, the wind at Site 2-A shifted to southwest about half way through the 1000-1100 hrs sampling; from Site 2-B, a steam plume at the refinery appeared to be heading towards the northeast at 1015 and towards the east from 1032 on, although it was difficult to judge direction from our vantage point. A strong refinery odor was detectable at Site 2-B throughout the sampling.

Downwind samples were taken between 1315 and 1415 hrs at Sites 2-C and 2-D. The wind was steadily from the west and southwest, and a strong refinery odor was present at Site 2-D. During the hour, 37 vehicles passed Site 2-D. After the samples were taken, the wind shifted to northwest. We waited for over an hour to see whether this new pattern would stabilize. When it appeared that it would, we chose Site 2-E to be downwind. Samples were then taken from 1610 to 1710 hrs at Sites 2-D and 2-E. During the hour, the wind direction changed frequently, varying from NW to WSW. When the wind was from the northwest, a strong chemical odor, such as that of an ether, was detected. It was assumed that when the wind was from the west or west-southwest, Site 2-D would "see" most of the refinery emissions; when the winds were from the northwest, then Site 2-E would be the primary receptor.

6.3.2.3 Special Sampling Provisions

In order to determine the potential for breakthrough, two impingers were connected in series; Sample No. 2-7 was the "front" impinger and No. 2-1 was the "backup."

6.3.2.4 Results and Discussion

Results of the sampling and analysis are presented in Table 6.3-4. Sample No. 2-1, which was from the backup impinger at Site 2-B, was

Table 6.3-4

RESULTS OF ANALYSES OF REFINERY SAMPLES

Sample Number	Mass[a] (μg)	Volume (m³)	Temperature (°C)	Raw Concentration (μg/m³)	Adjusted Concentration (ppb)	Comments
2-1	-	0.0597	25.8	-	-	Sample lost by ERT.
2-2	0.70	0.0423	26.5	16.55	13.6	
2-3	0.48	0.0567	22.0	8.47	6.8	
2-4	0.31	0.0543	30.8	5.71	4.8	
2-5	0.37	0.0609	30.5	6.08	5.1	
2-6	0.87	0.0531	23.8	16.38	13.3	
2-7	1.10	0.0597	25.8	18.43	15.1	

[a]provided by ERT.

6-18

inadvertently lost during analysis. Concentrations ranged from 4.8 to 15.1 ppb. Figure 6.3-4 shows an outline of the refinery, along with measured concentrations at the sampling sites (indicated by dots). Arrows show the range and average wind directions during each sampling interval. The origin of the arrows is at the approximate center of the major combustion and refining activity.

During the 10 - 11 a.m. sampling, Sites 2-A and 2-B were clearly upwind and downwind, respectively. Although the downwind concentration was slightly higher, the refinery does not appear to have contributed significantly to ambient formaldehyde levels. It should be noted, in this and in all the other cases for the refinery, that the downwind sampling location may not have been optimal; to determine a point of maximum concentration resulting from a multiple source as complex as this would have required extensive modeling. However, the placement of Site 2-B in a downwind residential area did provide us with a measure of public exposure.

For the 1315-1415 hrs sampling, both sites were downwind of the major sources within the refinery. On the average, Site 2-C was nearly on the centerline of any effluent plume. Measured formaldehyde concentrations were rather low. Again, the sites may not have been optimally located. During the final sampling, the wind direction varied considerably. Sites 2-D and 2-E were both downwind of the major sources. Despite being considerably off the mean plume centerline, Site 2-E had almost twice the formaldehyde concentration of Site 2-D.

In conclusion, formaldehyde concentrations in areas near the oil refinery are not significantly above background. Whether the concentrations measured are the maximum resulting from the refinery's contribution cannot be determined from our results.

6.3.3   Southern California Edison Electric Power Plant, Ormond Beach

"Hot spot" sampling was conducted downwind of Southern California Edison's Ormand Beach Power plant near Pt. Mugu, Ventura County, on 20 January 1983.

15.1

13.6

1000 - 1100

● 5.1

● 4.8

1315 - 1415

● 13.3

6.8

1610 - 1710
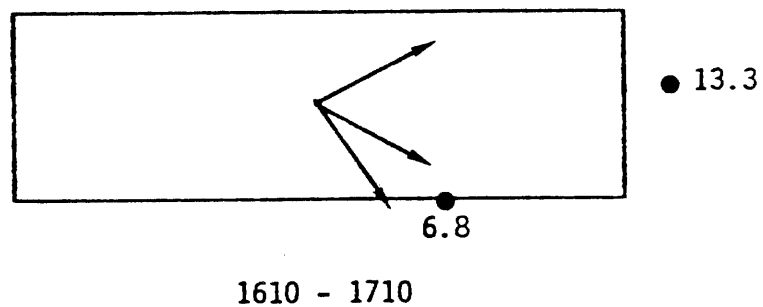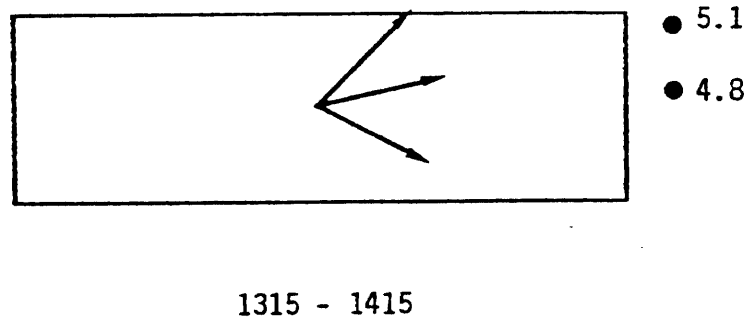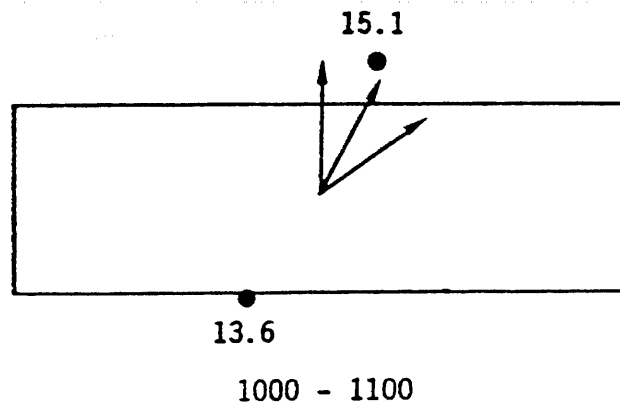
Table 6.3-4. Formaldehyde Concentrations (ppb) Measured Around the Mobil
Oil Refinery in Torrance. Arrows Indicate Range and Mean of
Wind Directions During Sampling.

6.3.3.1 Sampling Sites

Figure 6.3-5 shows the sampling sites, while Table 6.3-5 reports the sampling schedule. At around 1400 hrs wind speed was about 3 m/sec (10 ft/sec) from the west. Before conducting the sampling, we ran the Gaussian dispersion model PTMAX, using stack parameters provided by the Ventura County Air Pollution Control District (Duvall, 1983) to determine the distance of maximum ground-level concentration for various combinations of wind speed and atmospheric stability class. Table 6.3-6 shows the modeling results. The stability class on the afternoon of the sampling day was determined from National Climatic Center tables (Doty et al., 1976) and measured wind speed to be C. The point of maximum likely ground-level HCHO concentration was then determined to be 9 km (5.6 miles) due east of the power plant.

Site 3-A was on the east shoulder of Las Posas Road, about 9 km (5.6 miles) due east of the power plant. The site is surrounded by flat, open fields, but a line of tall trees about 5 km (3.1 miles) due west obscured a view of the power plant stacks. Jets could be seen taking off and landing at Pt. Mugu Naval Air Station, about 4 km (2.5 miles) to the southwest. The sample inlet was placed about 2 m (6.6 ft) from the road, about 0.6 m (2 ft) off the ground. Traffic was moderate with about 285 vehicles passing by during the sampling period. Passage of these vehicles at about 72 km/hr (45 miles/hr) created strong localized gusts at the sampling site.

Site 3-B was on the south shoulder of Hueneme Road about 9 km (5.6 miles) northeast of the power plant. The site is bounded by flat, open fields to the north, east and south. Tall trees about 600 m (2,000 ft) to the southwest prevented a clear view of the power plant stacks. The sampler inlet was placed above the roof of an automobile about 2.3 m (7.5 ft) above the ground and 3 m (10 ft) from the road. Wind speed and direction were measured at this site with the Climatronics portable weather station. In 15 minutes, 107 vehicles passed by at an average speed of about 72 km/hr (45 miles/hr), creating gusts near the sample inlet.
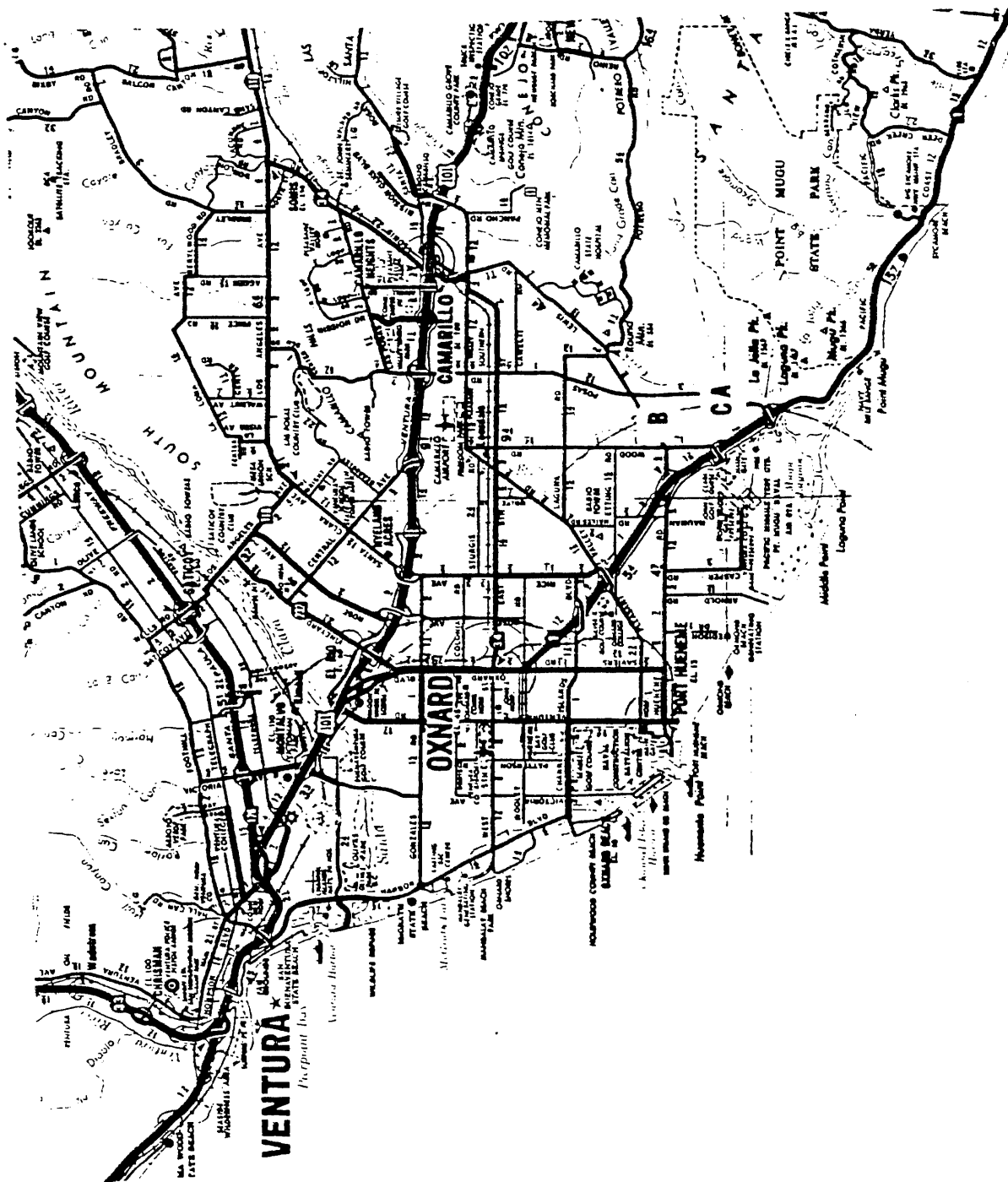
Figure 6.3-5. Sampling Sites Downwind From the Ormond Beach Generating Station.

Table 6.3-5

FORMALDEHYDE SAMPLING SCHEDULE AT ORMOND BEACH

Site No.[a]	Location	Sampling Times (hours of day)	Upwind/Downwind	Sample Numbers	Comment
3-A	Las Posas Road (east side)	1450 - 1550	Downwind	6-1	
3-B	Hueneme Road	1452 - 1552	Downwind	6-2	
3-C	Las Posas Road (west side)	1641 - 1720	Downwind	6-3	Sampling terminated when wind shifted

[a] Shown in Figures 6.3-5 and 6.3-6 as A, B, and C.

Table 6.3-6

RESULTS OF PTMAX RUN FOR ORMOND BEACH POWER PLANT

Stability Class	Wind Speed (m/sec)	Max.Conc. (g/cu. m)	Dist. of Max. (km)	Plume Height (m)
	0.5	a	a	2914.5[b]
	0.8	7.2456×10^{-7}	1.790	1850.2[b]
	1.0	7.8308×10^{-7}	1.619	1495.4[b]
A	1.5	8.9424×10^{-7}	1.352	1022.3[b]
	2.0	9.7356×10^{-7}	1.194	785.8[b]
	2.5	1.0328×10^{-6}	1.086	643.9[b]
	3.0	1.0775×10^{-6}	1.008	549.3[b]
	0.5	a	a	2914.5[b]
	0.8	1.9846×10^{-7}	10.109	1850.2[b]
	1.0	2.3242×10^{-7}	8.327	1495.4[b]
	1.5	3.0663×10^{-7}	5.877	1022.3[b]
B	2.0	3.6934×10^{-7}	4.620	785.8[b]
	2.5	4.2303×10^{-7}	3.850	643.9[b]
	3.0	4.6942×10^{-7}	3.330	549.3
	4.0	5.4521×10^{-7}	2.667	431.0
	5.0	6.0385×10^{-7}	2.263	360.0
	2.0	2.3307×10^{-7}	11.267	785.8
	2.5	2.7613×10^{-7}	9.055	643.9
	3.0	3.1500×10^{-7}	7.606	549.3
	4.0	3.8156×10^{-7}	5.833	431.0
C	5.0	4.3576×10^{-7}	4.787	360.0
	7.0	5.1624×10^{-7}	3.616	278.9
	10.0	5.8884×10^{-7}	2.760	218.1
	12.0	6.1631×10^{-7}	2.434	194.5
	15.0	6.3828×10^{-7}	2.112	170.8

Table 6.3-6

(Continued)

Stability Class	Wind Speed (m/sec)	Max.Conc. (g/cu. m)	Dist. of Max. (km)	Plume Height (m)
	0.5	a	a	2914.5[b]
	0.8	a	a	1850.2[b]
	1.0	a	c	1495.4[b]
	1.5	2.6838×10^{-8}	c	1022.3[b]
	2.0	4.0480×10^{-8}	c	785.8[b]
	2.5	5.5204×10^{-8}	72.104	643.9[b]
D	3.0	7.0532×10^{-8}	52.622	549.3[b]
	4.0	1.0162×10^{-7}	33.988	431.0[b]
	5.0	1.3008×10^{-7}	24.803	360.0[b]
	7.0	1.7821×10^{-7}	15.827	278.9[b]
	10.0	2.3365×10^{-7}	10.497	218.1[b]
	12.0	2.6045×10^{-7}	8.675	194.5
	15.0	2.8747×10^{-7}	7.031	170.8
	20.0	3.1211×10^{-7}	5.523	147.2
	2.0	3.9999×10^{-7}	29.420	237.3[b]
	2.5	3.8081×10^{-7}	26.307	225.7[b]
	3.0	3.6465×10^{-7}	24.059	216.9[b]
	4.0	3.3850×10^{-7}	20.977	204.0[b]
	5.0	3.1275×10^{-7}	19.152	194.9[b]
	2.0	a	a	209.9[b]
	2.5	a	a	200.3[b]
	3.0	1.2958×10^{-7}	77.856	193.0[b]
	4.0	1.2259×10^{-7}	67.507	182.3
	5.0	1.1669×10^{-7}	60.671	174.7

[a] The distance to the point of maximum concentration is so great that the same stability is not likely to persist long enough for the plume to travel this far.

[b] The plume is of sufficient height that extreme caution should be used in interpreting this computation as this stability type may not exist to this height. Also, wind speed variations with height may exert a dominating influence.

[c] No computation was attempted for this height as the point of maximum concentration is greater than 100 kilometers from the source.

Site 3-C was located about 15 m (49 ft) west of Las Posas Road in an flat open field. The site was about 9 km (5.6 miles) due east of the power plant and 23 m (75 ft) west of Site 3-A. This site was selected because it was downwind from the power plant and was away from busy Las Posas Road. The geographical descriptions given for Site 3-A also apply for Site 3-C except that the sample inlet was situated about 2.4 m (8 ft) below road level in the open field. Wind direction and wind speed were measured at this site.

6.3.3.2 <u>Sampling Conditions</u>

Skies were clear with temperatures ranging from $20^{o}C$ at 1400 to $11^{o}C$ at 1720 hrs. Wind speed and direction readings were taken around 1400 hrs on Arnold Road (1.6 km east of the power plant), from 1500 to 1600 hrs at Site 3-B and from 1640 to 1720 hrs at Site 3-C. At 1500 hrs wind speed was 3 m/sec (10 ft/sec) from the northwest (310°). Downwind samples were taken at Sites 3-A and 3-B from 1450 to 1550 hrs. During this period, wind speed stayed fairly constant but wind direction became more westerly. Due to changing wind direction, Site 3-A may have been considerably off the centerline of the "plume" of emissions for the power plant. Wind speed at Site 3-C varied between 2.5 and 3 m/sec from the west (270°). A third downwind sample was taken at Site 3-C from 1640 to 1720 hrs. Because of the wind direction, the site was also downwind of Pt. Magu Naval Air Station, where jets were continually landing and taking off. At around 1716 hrs the sun went down and winds shifted to the southeast. Sampling was terminated shortly thereafter.

6.3.3.3 <u>Results and Discussion</u>

Results of the sampling and analysis are shown in Table 6.3-7. As seen in Figure 6.3-6, the Pacific Ocean was immediately upwind of the power plant for most of the sampling; there was thus no need to take an upwind sample. Formaldehyde concentrations varied from 6.3 to 17.8 ppb. The higher reading at Site 3-C may be due to the fact that, as may be noted in the figure, offline distance from the mean plume was smaller during the second sampling interval.

Table 6.3-7

RESULTS OF ANALYSES OF ORMOND BEACH SAMPLES

Sample Number	Mass[a] (μg)	Volume (m³)	Temperature (°C)	Raw Concentration (μg/m³)	Adjusted Concentration (ppb)
6-1	0.57	0.0690	16.5	8.26	6.4
6-2	0.46	0.0573	19.0	9.03	6.3
6-3	1.06	0.0448	12.0	23.66	17.8

[a]Provided by ERT.

6.3

● B

● A
6.4

OCEAN

1450 - 1550

17.8

● A,C

OCEAN

1641 - 1720
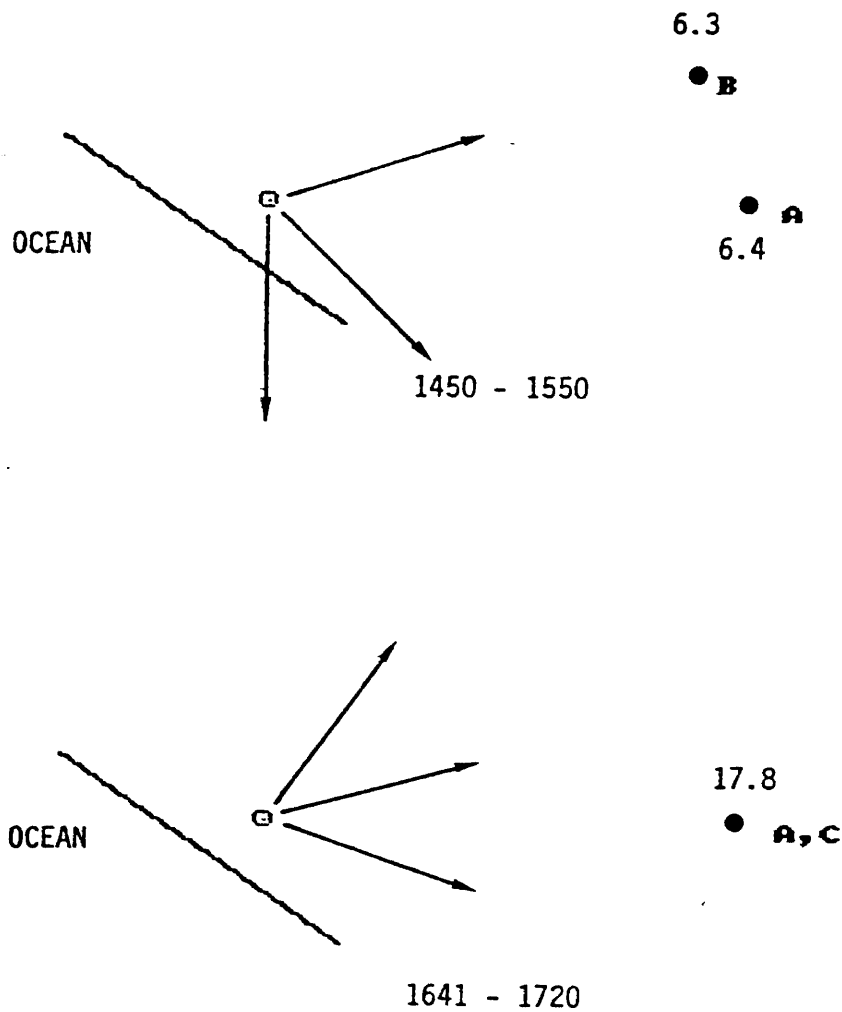
Figure 6.3-6. Formaldehyde Concentrations (ppb) Measured Downwind From the
Southern California Edison Electric Power Plant at Ormond
Beach. Arrows Indicate Range and Mean of Wind Directions
During Sampling.

The large portion of the time when the sampling sites were off the plume center line probably led to the low concentrations, despite the choice of optimum distance from the source. The extent to which formaldehyde in highway traffic and Navy jet exhaust contributed to the measured values is unknown. Since both these interfering factors will be present during those hours of the day when winds are onshore, it is doubtful whether the contribution of the power plant can ever be unambiguously established.

6.3.4 Reichhold Chemicals, Inc., South San Francisco

"Hot spot" sampling was conducted at Reichhold Chemicals, Inc. (RCI) in South San Francisco on 11 February 1983.

6.3.4.1 Sampling Sites

Figure 6.3-7 shows the sampling sites, while Table 6.3-8 reports the sampling schedule. All wind speed and wind direction designations were made by visual observation using a compass. At 1100 hrs, winds were very light, blowing from the northeast (30°). Site 4-A was selected as a morning upwind location on the Southern Pacific Railroad right-of-way, about 250 ft (76 m) directly northeast of RCI. The site is bounded by a manufacturer of fabricated steel products and a muffler shop on the west, a mineral processing company on the east and several other small to medium sized industrial establishments to the north and south. The sample inlet was placed 2 ft (0.6 m) off the ground on the east shoulder of the railroad tracks.

Site 4-B was several hundred feet southwest of RCI on Maple Avenue, about 400 ft (122 m) north of Browning Way. The site is bounded by a small winery on the west and an abandoned E.I. du Pont de Nemours facility approximately 300 ft (91 m) to the southeast. Several other small industrial and commercial establishments are located in the immediate vicinity. The sampler inlet was placed atop an automobile about 7 ft (2.1 m) from the ground.
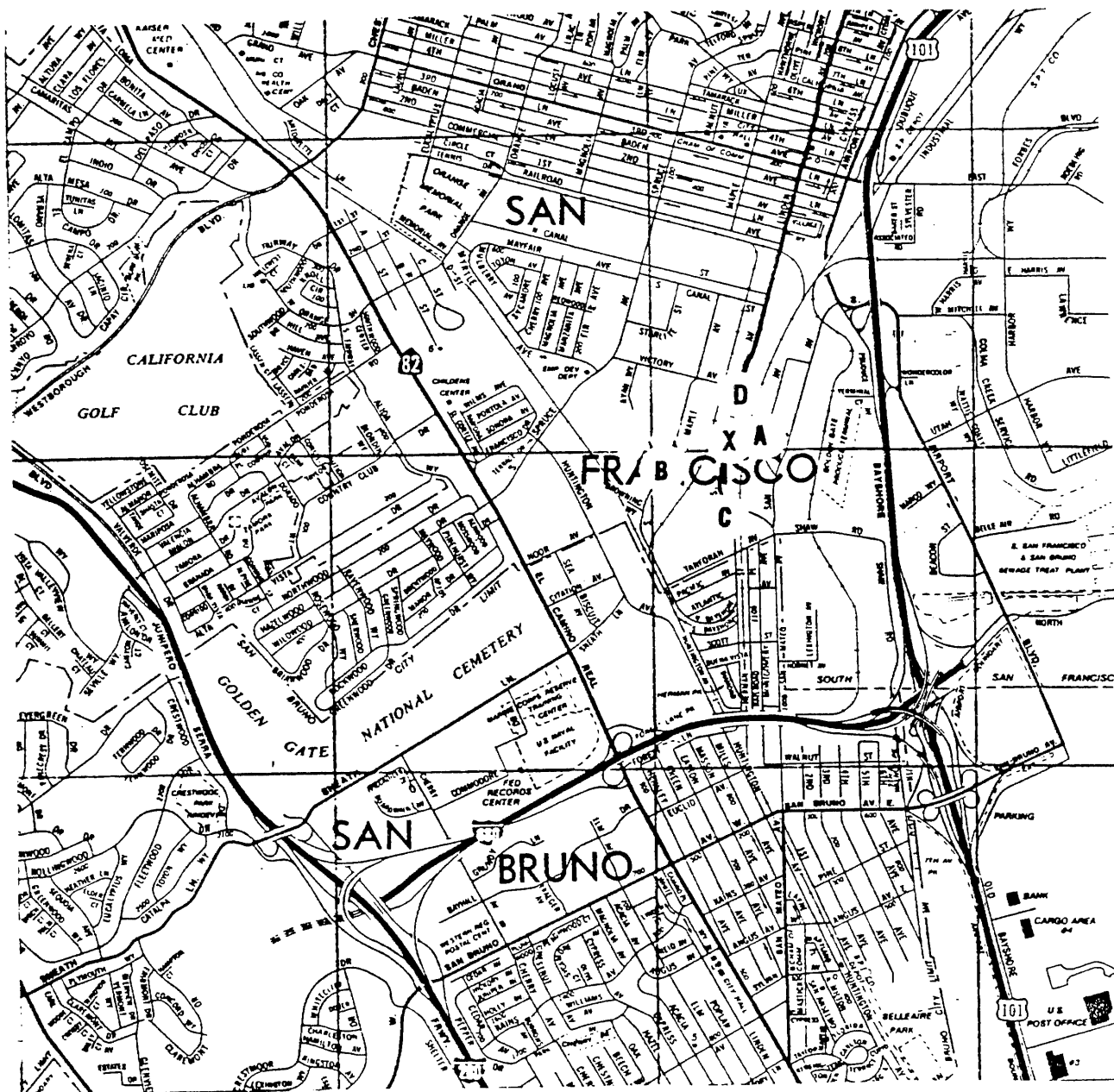
Figure 6.3-7. Sampling Sites Around the Reichhold Chemicals, Inc. Resin
Plant (X) in South San Francisco.

Table 6.3-8

FORMALDEHYDE SAMPLING SCHEDULE AT RESIN PLANT

Site No.[a]	Location	Sampling Times (hours of day)	Upwind/ Downwind	Sample Numbers	Comment
4-A	SPRR right-of-way	1110-1210	Upwind	9-3	Became downwind after 1130 hrs
4-B	Maple Avenue near Browning Way	1110-1125	Downwind	9-2	Measurement aborted when wind shifted
4-C	Dollar Avenue near S. Linden Avenue	1400-1500	Upwind	9-4	
4-D	S. Linden Avenue and Victory Avenue	1402-1502	Downwind	9-1	

[a] Shown in Tables 6.3-7 and 6.3-8 as A, B, C, and D.

At 1400 hrs light to moderate winds were blowing from the south (190°). Site 4-C was located on Dollar Avenue about 50 ft (15 m) south of South Linden Avenue and about 1200 ft (370 m) due south (upwind) of RCI. The site was bounded by an abandoned E.I. du Pont de Nemours facility on the west, railroad tracks on the east and small industrial establishments on the north and south. The sampler inlet was placed about 2 ft (0.6 m) off the ground on the west sidewalk of Dollar Avenue.

Site 4-D was 600 ft (180 m) due north (downwind) of RCI on the southwest corner of the intersection of South Linden Avenue and Victory Avenue. The site was located on a heavily travelled two-lane road frequented by large diesel trucks and other passenger vehicles, and was bounded by a printing shop, a wrecking shop and a paint factory outlet (non-manufacturing) on the west and south, and a construction shop on the east. The sampler inlet was located on the roof of an automobile about 7 ft (2.1 m) off the ground.

6.3.4.2 Sampling Conditions

Problems occurred during transport of the reagent and organic solvent vials by jet aircraft to the sampling site. The pressure differential between the sample vial contents and the unpressurized baggage compartment air resulted in considerable leakage of fluid. Remaining reagent and solvent were scavenged to insure that at least 10 ml of DNPH reagent and 5 ml of solvent per sample run were used. A sample blank was subsequently prepared to determine if contamination had occurred during and after transport to the sampling site.

Upwind and downwind samples were to be taken between 1110 and 1210 hrs at Sites 4-A and 4-B, respectively. Skies were overcast. Winds were very light and generally blew from the northeast. Wind direction changed many times during this sampling period. At 1125 hrs, Sites A and B were no longer upwind and downwind, respectively; winds began blowing from the south. Sampling at Site B was terminated shortly thereafter. It is highly unlikely that the Site B sample accurately represents downwind emissions of RCI.

From 1400 to 1500 hrs upwind and downwind readings were taken at Sites C and D, respectively. Moderate winds blew directly from the south. Skies were very cloudy and air temperature was about 60°F (15.6°C). Traffic was heavy near Site D but strong odors from RCI were evident during the entire hour. Wind direction did not change during this period.

6.3.4.3 Results and Discussion

Results of the sampling and analysis are shown in Table 6.3-9. The field blank contained 0.23 μg of formaldehyde, indicating some contamination. This amount was not subtracted from the values shown in Table 6.3-9, since it is not known to what extent each of the reagent and/or organic solvent vials was contaminated.

The locations of the sampling sites and measured concentrations are shown in Figure 6.3-8. Although the morning sampling was terminated early because of a wind shift, the formaldehyde concentration downwind from the plant was higher than the upwind value. In the afternoon, when the upwind-downwind pattern was clearly established and steady, the downwind concentration was four times that measured upwind. The facility therefore appears to be contributing formaldehyde to the atmosphere of the surrounding area.

6.3.5 Shopping Mall

On 3 February 1983 air samples were collected inside a large enclosed shopping mall in the Los Angeles area.

6.3.5.1 Sampling Site

Two one-hour samples were collected on an open stairway connecting the lowest two levels of the mall. In order to be as unobtrusive as possible, we placed the sampling apparatus in a cardboard box. Since cardboard could contain residual formaldehyde, a 3-ft section of Teflon tubing was connected to the impinger inlet and suspended from the stairway structure. The inlet point was thus about 15 ft (5 m) above the main floor of the mall.

Table 6.3-9

RESULTS OF ANALYSES OF RESIN PLANT SAMPLES

Sample Number	Mass[a] (μg)	Volume (m³)	Temperature (°C)	Raw Concentration (μg/m³)	Adjusted Concentration (ppb)	Comments
9-1	2.37	0.0612	17.0	38.73	30.4	Strong odor noted.
9-2	0.92	0.0170	16.0	• 56.79	42.2	Variable winds.
9-3	2.54	0.1260	23.5	20.16	16.3	
9-4	0.59	0.0624	18.5	9.46	7.5	
9-5	0.23	-	-	-		Field Blank

[a] Provided by ERT.

```
        ⊙●A  16.3

              N
              ↑
42.2 ●B


      1110 - 1210



      ◗ 30.4


      ⊙

              N
              ↑

   c ●7.5

   1400 - 1500
```
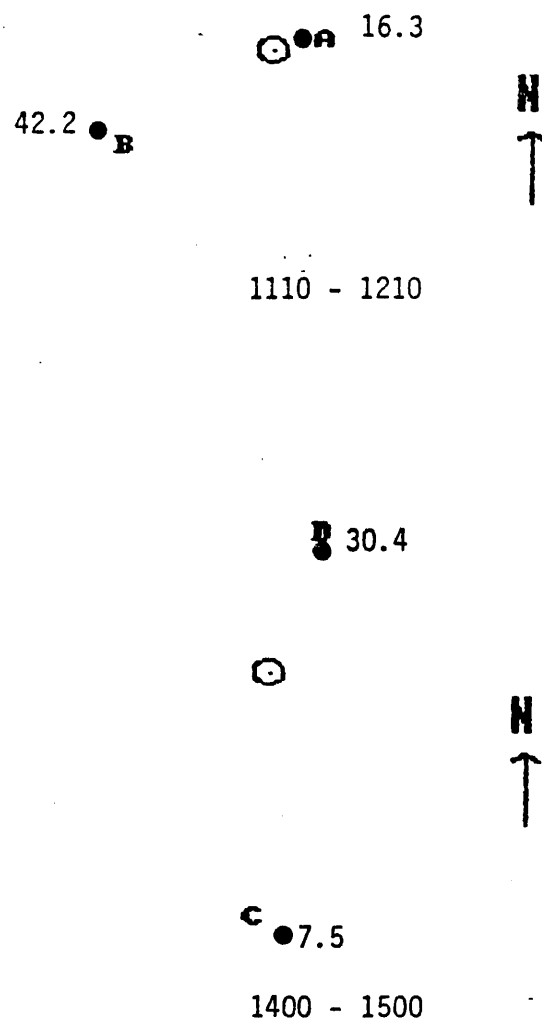
Figure 6.3-8.   Formaldehyde Concentrations (ppb) Around the Reichhold
                Chemicals, Inc. Resin Plant in South San Francisco. The
                Facility is Indicated by a Circle.

6.3.5.2 Sampling Conditions

One-hour samples were collected starting at 1114 and 1220 hrs.

6.3.5.3 Results and Discussion

The ambient formaldehyde concentrations at the sampling site at 1114 and 1220 hrs were 25.5 and 25.0 ppb, respectively. These values are lower than those for 63 of the 70 (90 percent) residences at which we conducted passive monitor sampling.

6.4   SPECIES COMPOSITION OF "HOT SPOT" SAMPLES

Table 6.4-1 shows the carbonyl species breakdown of air samples collected at Los Angeles International Airport, the oil refinery and the Ormond Beach power plant. Concentrations at or below the lower detection limit (as determined for each species by ERT) are considered to be zero. The table shows, for each case, the ratio between the measured concentration and the corresponding detection limit. Higher molecular weight carbonyls were present at a significant levels only in the vicinity of Los Angeles International Airport.

6.5   REFERENCES

Doty, S.R., B.L. Wallace and G.C. Holzworth. 1976. A climatological analysis of Pasquill stability catagories based on "STAR" summaries. National Oceanic and Atmospheric Administration, Environmental Data Service, National Climatic Center, Asheville, NC.

Duvall, Keith, Ventura County Air Pollution Control District, Ventura, CA. Personal communication (4 January 1983).

Smith J.R. 1979. "Estimating overall sampling train efficiency," Journal of the Air Pollution Control Association 29(9):969-970.

Wright, Barbara, Manager, Chemical Studies Section, Environmental Chemistry Division, Environmental Research and Technology, Inc., Westlake Village, CA. Personal communication (10 February 1983).

Table 6.4-1

SPECIES COMPOSITION OF "HOT SPOT" SAMPLES
(All concentrations in ppb)

Sample No. Site	1-7 LAX		2-4 Refinery		6-1 Power Plant	
Species	Conc.	Conc./LD	Conc.	Conc./LD	Conc.	Conc/LD
Formaldehyde	18.9	8.0	8.1	2.6	5.0	2.2
Acetaldehyde	5.8	36.0	3.9	18.5	ND	0
Acetone	6.1	4.5	6.3	3.6	2.0	1.6
Acrolein	ND[a]	0	ND	0	ND	0
Propanal	0.6[b]	4.5	0.3[b]	2.0	ND	0
MEK	1.3[b]	0.9	1.9[b]	1.0	1.3[b]	0.9
Butanal	0.6	4.3	0.2[b]	1.0	ND	0
Benzaldehyde	0.3	2.3	0.2[b]	1.0	ND	0
Hexanal	ND	0	ND	0	0.1[b]	0.75
Total	32.3		18.6		7.0	

[a]ND = Below lower detection limit

[b]Concentration at or near detection limit and should be considered zero.

7.0
AMBIENT AND COMMUTER EXPOSURE SAMPLING

7.1   SELECTION OF SAMPLING SITES AND COMMUTER ROUTES

The purposes of this part of the field measurement program were (1) to supplement the existing data base on ambient formaldehyde concentrations, (2) obtain data on commuter exposure, and (3) ascertain relationships, if any, between ambient concentrations of ozone, carbon monoxide and formaldehyde. As documented by Hoggan et al. (undated), the highest monthly averages of daily one-hour maximum ozone concentrations in the South Coast Air Basin occur in June, July and August; a secondary peak occurs in October in some locations. Maximum monthly average carbon monoxide concentrations, on the other hand, occur in November and January. It was therefore decided to measure ambient HCHO during two distinct seasons. In the winter, direct emissions from combustion sources would be the chief contributor. In summer, photochemical processes would be the main source of formaldehyde.

In order to maximize the comparability of HCHO, O_3 and CO measurements, it was decided to colocate our samplers with those of the South Coast Air Quality Management District. After reviewing CO and O_3 data for all the stations in the basin, we decided to conduct our formaldehyde sampling at the Lennox, Pico-Rivera and Azusa monitoring stations. The Lennox station, which was used only for our winter sampling, experiences some of the highest carbon monoxide concentrations in the basin. The Azusa station, which was used only for our summer sampling, has the highest O_3 concentrations among stations in the Los Angeles Basin and San Gabriel Valley. The Pico-Rivera monitoring station was used during both sampling seasons. The relatively low concentrations of CO and O_3 observed there were expected to extend the range of values to be considered in the correlation analysis.

Figure 7.1-1 shows the SCAQMD monitoring stations and the routes used for the commuter exposure sampling. The commuter routes were designed so that the test automobile was within the areas of influence of the two

L = Lennox Station
P = Pico Rivera Station
A = Azusa Station
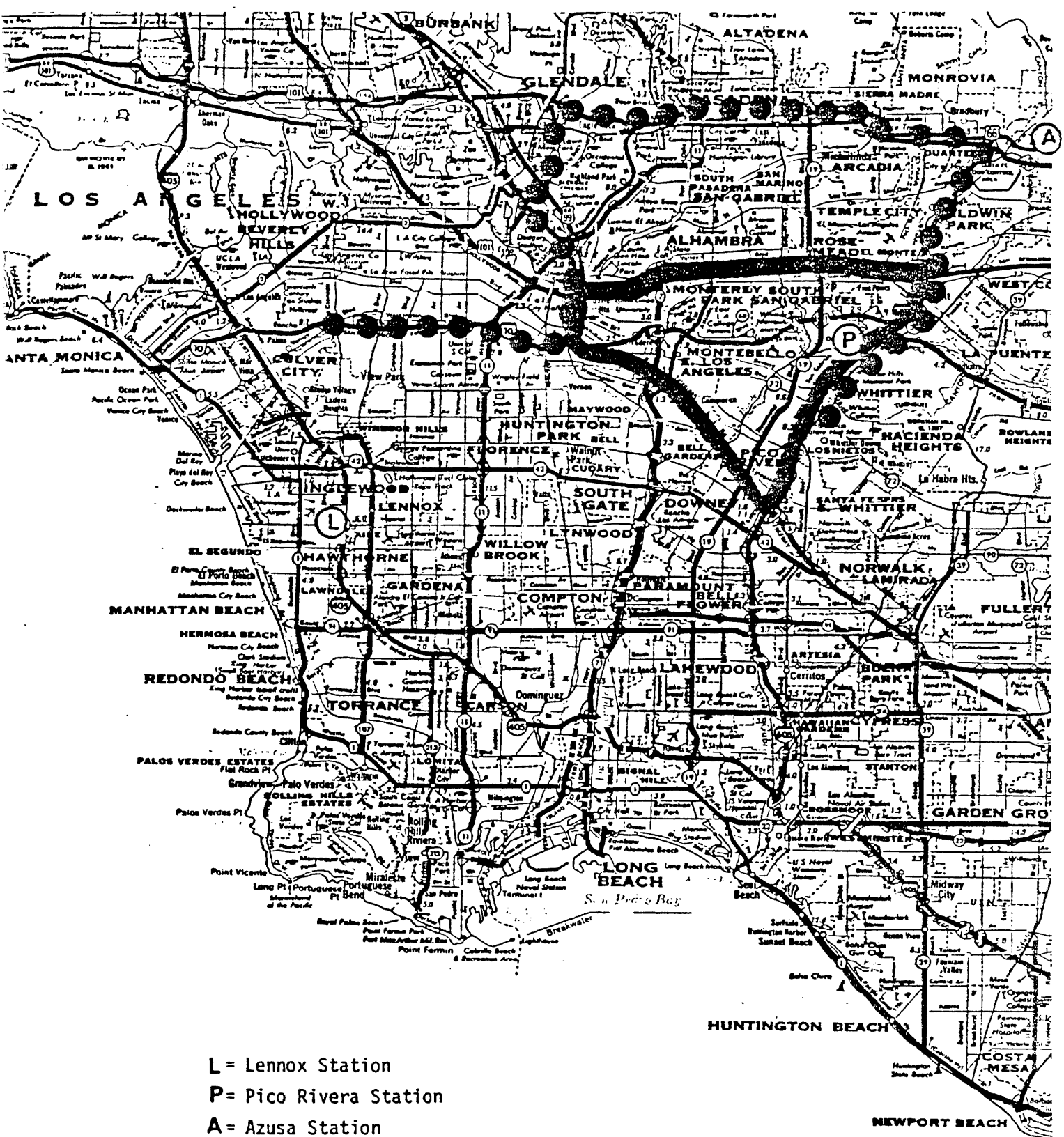
Figure 7.1-1.   Location of South Coast Air Quality Management District
                Stations Used For Ambient Sampling and Routes Used For
                Commuter Sampling.

monitoring stations (Lennox and Pico-Rivera in winter and Azusa and
Pico-Rivera in summer).

7.2 METHODS AND RESULTS

7.2.1 Field Protocols

The impinger sampling method described for the "hot spot" sampling
(see Section 6.2) was also used for the winter ambient and commuter exposure
sampling. In the summer, the method was revised slightly; instead of mixing
the 2,4-DNPH/hydrochloric acid and organic solvent solutions in the impingers
at the time of sampling, we used impingers containing pre-mixed reagents.
For the commuter sampling, the pump and ringstand were set up in the front
seat, with the inlet at passenger breathing level. Windows on both the
driver and passenger side were left open.

Winter sampling (fixed-site and commuter) was conducted on 13, 14
and 19 January 1983. Summer sampling at the SCAQMD monitoring stations took
place on 26 May and 14 and 16 June 1983; commuter sampling was conducted on
26 May and 16 June only. For the monitoring stations, sampling times were
chosen to correspond to historical maximum carbon monoxide and ozone
concentrations; commuter sampling times generally coincided with morning and
afternoon rush hours.

7.2.2 Results and Discussions

Formaldehyde concentrations measured at the SCAQMD monitoring
stations and in the commuter automobile are reported in Table 7.2-1. Hourly
average fixed-site concentrations ranged from 4.3 to 33.3 ppb in winter and
from 2.0 to 23.3 ppb in the summer. Commuter exposures in winter and summer
ranged from 10.7 to 91.5 ppb and from 11.3 to 22.5 ppb, respectively.

Examination of pooled data (i.e. for all hours sampled) from each
of the stations in each season by a two-sided t test showed that the only
statistically significant difference in mean HCHO concentrations ($p < 0.05$)
is that between the Azusa and Pico-Rivera stations in summer. These means

Table 7.2-1

RESULTS OF FIXED SITE STATION AND COMMUTER EXPOSURE SAMPLING
(Formaldehyde concentrations in ppb)

Date	Nominal Hour	Lennox Station	Commuter	Pico-Rivera Station	Commuter	Azusa Station
1-13-83	0700		37.4			
	0800	11.6	48.4	6.0		
	0900	11.7		11.0		
					Not measured	
	1400	15.0				
	1500	7.3				
	1600		30.5			
	1700		39.4			
1-14-83	0800	11.7	91.5	16.0	Not measured	
	0900	8.5		33.3		
1-19-83	0700		22.9			
	0800		10.7	18.2		
	0900	18.2		·10.6		
					Not measured	
	1400	10.9		9.5		
	1500	16.0		4.3		
	1600		31.1			
	1700		27.3			
5-26-83	1200			3.9		5.6
	1300			6.7	12.9	12.7
	1400	Not measured		5.2		14.8
	1500					
	1600			6.5	11.3	19.4
	1700					
6-14-83	1200			8.2		14.6
	1300			13.5		12.2
	1400	Not measured		17.0		23.3
	1500			7.4		15.9
	1600					
6-16-83	1200			9.8		11.7
	1300				21.1	10.2
	1400	Not measured		8.5		7.6
	1500			2.0		
	1600			4.8	22.5	13.9

were 13.5 and 7.8 ppb, respectively (t = 3.112, d.f. = 22). A similar analysis showed that the mean commuter exposure was higher in winter than at either of the monitoring stations but higher in summer only with respect to the Pico-Rivera station. (See Table 7.2-2.) Concentrations at each station were matched by hour and date to see whether those from one were significantly higher or lower than those from the other. Use of a sign test (Dixon and Massey, 1969) showed that, while most Lennox values were higher than those for Pico-Rivera in winter, and most Azusa values were higher than those for Pico-Rivera in summer, the numbers of positive and negative differences were not significantly different (p > 0.05). Sign tests also indicate that commuter exposure values were significantly higher than those for the Lennox and Azusa stations, but not those for Pico-Rivera.

Finally, results for each pair of stations were pooled by hour to determine whether any diurnal pattern of formaldehdye concentration was apparent. Figure 7.2-1 shows the mean and 95-percent confidence intervals for the winter and summer measurements. Given the rather high variance in the data, and the small number of samples, no diurnal pattern can be discerned.

7.3   CORRELATIONS BETWEEN FORMALDEHYDE, OZONE AND CARBON MONOXIDE

7.3.1   Analysis of Data From Previous Investigations

In Section 3.1.2, a multiple linear regression equation relating formaldehyde, ozone and carbon monoxide concentrations measured during a smog episode (ozone concentration > 0.1 ppm) in New Jersey was derived. Given the fairly close "fit" of the derived equation, an attempt was made to derive similar relationships with California data. A total of 239 combinations of HCHO, CO and O_3 values were obtained from four recent studies in the Los Angeles area (Tuazon et al., 1980; Hanst et al., 1982; Grosjean, 1982; and Grosjean et al., 1983). Table 7.3-1 summarizes the dates, locations and number of measurements used in the analysis.

Several multiple regression analyses were performed on the California data. Only a few attempts were made to incorporate a lead or lag

Table 7.2-2

COMPARISON OF MEAN COMMUTER AND FIXED-SITE FORMALDEHYDE CONCENTRATIONS
(Concentrations in ppb)

Fixed Site	Mean	Std. Dev	Commuter Exposure			
			Mean	Std. Dev	t[a]	d.f.
Lennox - Winter	12.3	3.51			3.297	16
			37.7	22.81		
Pico-Rivera - Winter	13.6	9.20			2.783	15
Pico-Rivera - Summer	7.8	4.15			1.198	14
			16.95	5.67		
Azusa - Summer	13.5	4.80			3.511	14

[a] These t statistics were used to compare the mean commuter exposure in each season with the corresponding fixed-site monitor means.

7-6
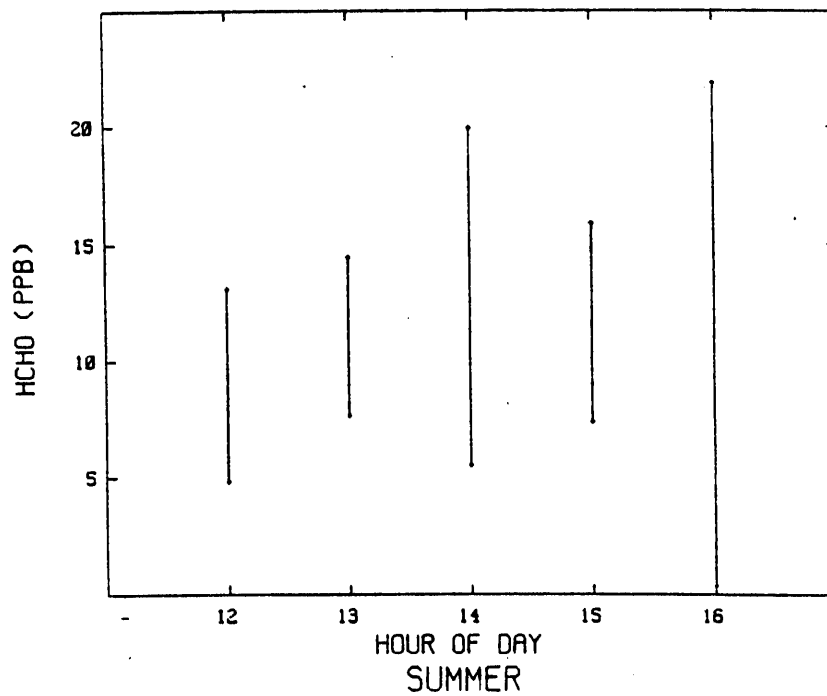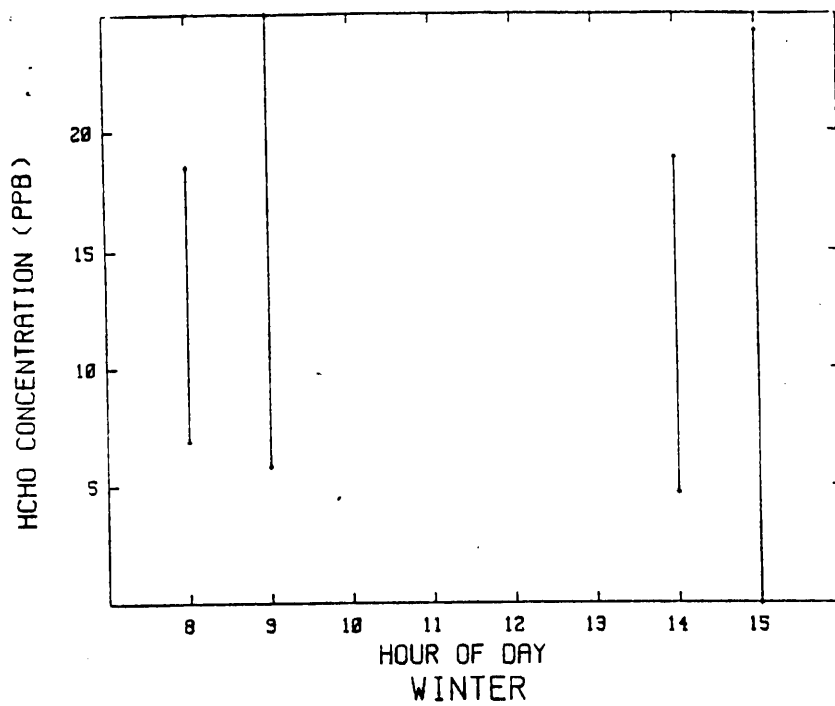
Figure 7.2-1. Variation in Ambient Formaldehyde Concentration With Time
of Day. (Error Bars Show 95-Percent Confidence Intervals.)

Table 7.3-1

DATA SETS USED FOR REGRESSION ANALYSIS ON LOS ANGELES AREA
FORMALDEHYDE, CARBON MONOXIDE AND OZONE CONCENTRATIONS

Data Set	Reference	Sampling Site(s)	Measurement Techniques	Date	No. Samples
1	Tuazon et al., 1980	Riverside	Infrared	July, October 1977	61
2	Hanst et al., 1982	Calif. State Univ., L.A.	Infrared	June 1980	25
3	Grosjean, 1982	Calif. State Univ., L.A.	HPLC-DNPH	June 1980	35
		Claremont	HPLC-DNPH	September, October 1980	64
4	Grosjean et al., 1983	Lennox	HPLC-DNPH	October 1980	16
		Azusa	HPLC-DNPH	October 1980	18
		Mobile Lab	HPLC-DNPH	July, August, September, October 1980	20

time between formaldehyde and ozone concentrations, since in most cases data were available for only a few consecutive hours. In addition, while the New Jersey data showed that formaldehyde peaks occurred three hours before ozone maxima, no clear lead or lag time could be discerned in the California data. Formaldehyde peaks were observed up to six hours before, and up to three hours after, those for ozone.

A multiple linear regression of the entire data set yielded the following equation:

$$[HCHO] = 2.40 \pm 0.43 \ [CO] + 39.3 \pm 8.5 \ [O_3] + 11.2 \pm 2.0 \qquad (7.3\text{-}1)$$

where HCHO, CO and O_3 are in ppb, ppm, and ppm, respectively. The overall correlation coefficient was 0.43, indicating limited usefulness in predicting formaldehyde concentrations.

Regression equations with higher statistical significance were obtained for individual locations. For example, the Claremont subset (64 measurements) yielded:

$$[HCHO] = 2.64 \ [CO] + 44.0 \ [O_3] + 7.6 \qquad (7.3\text{-}2)$$

The correlation coefficient for this equation was 0.71. Similarly, correlation coefficients for regression based on Riverside and Azusa data subsets were 0.77 and 0.81, respectively. The results of all these analyses suggest that reasonably good predictive equations may be derived for particular geographical areas, but that these results have very limited value for extending predictions to the rest of the state.

7.3.2 Analysis of SAI Field Data

Records of carbon monoxide and ozone measurements at the Lennox, Pico-Rivera and Azusa monitoring stations were obtained from the SCAQMD. Analysis of these data and our field sampling results showed a very poor correlation between formaldehyde and the two putative indicators. Figures 7.3-1 through 7.3-3 give examples of the variation of pollutant
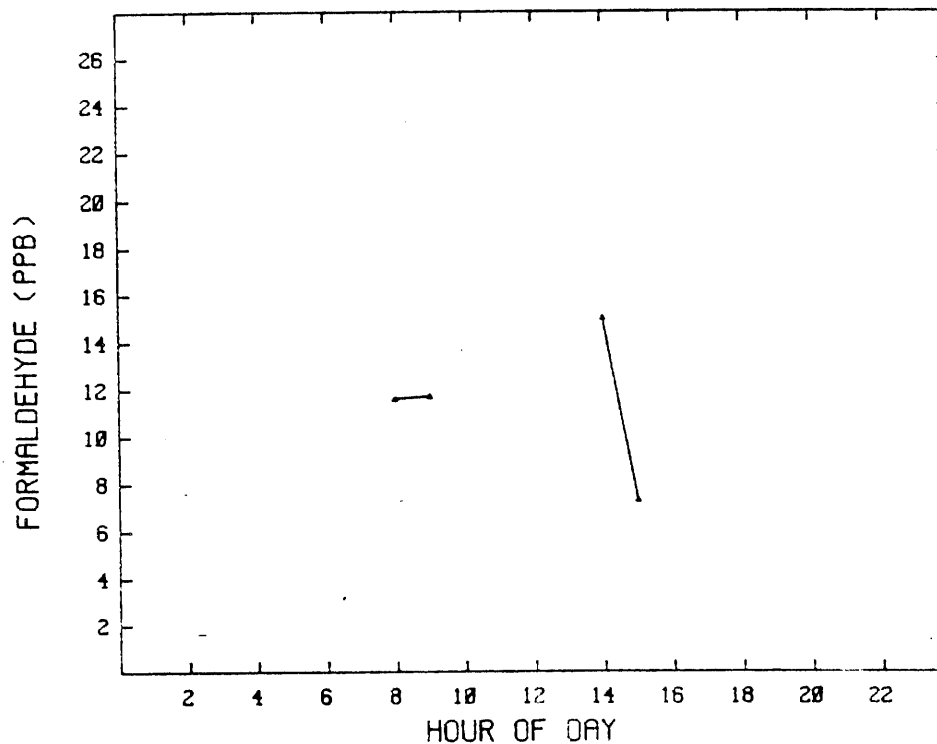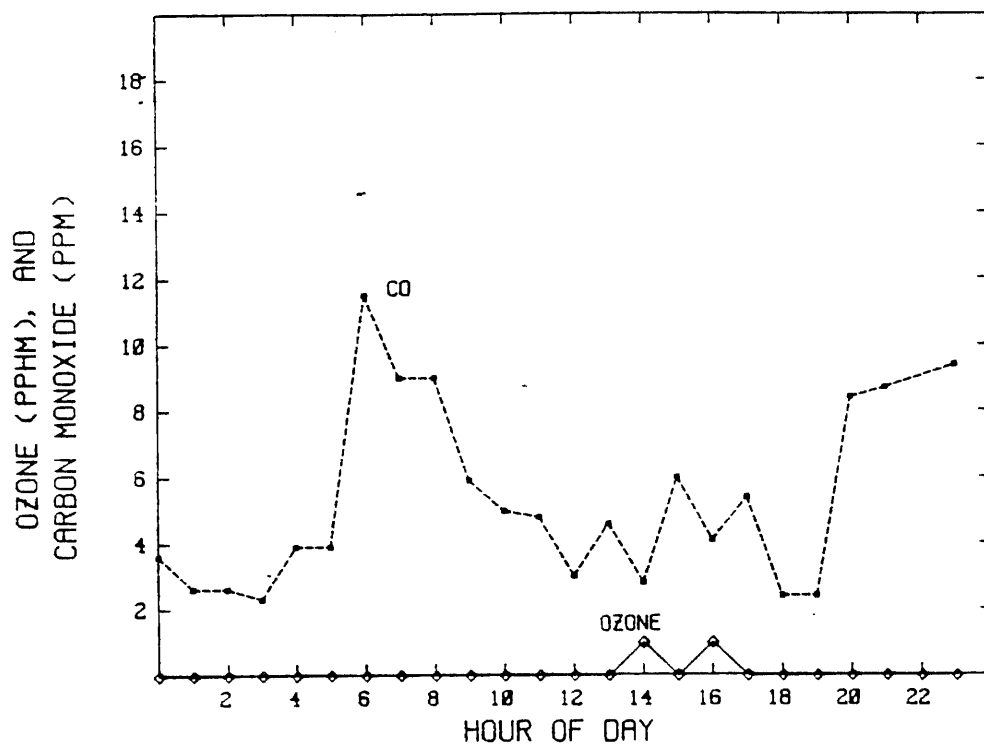
Figure 7.3-1. Carbon Monoxide, Ozone and Formaldehyde Concentr...
Measured at the South Coast Air Quality Managemen...
District's Lennox Monitoring Station, 13 January 198...
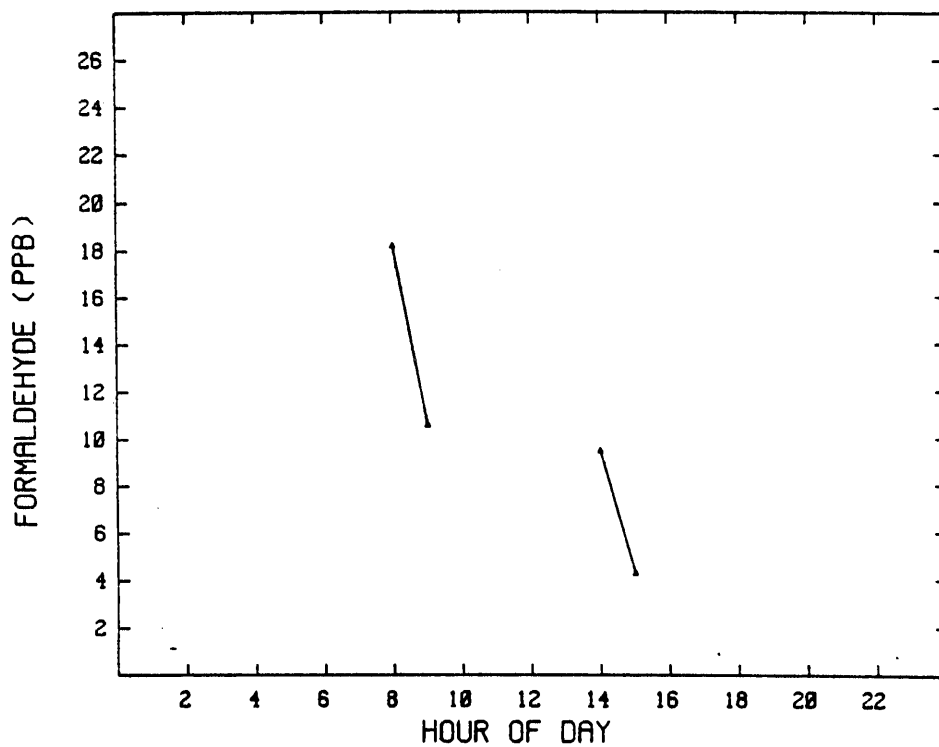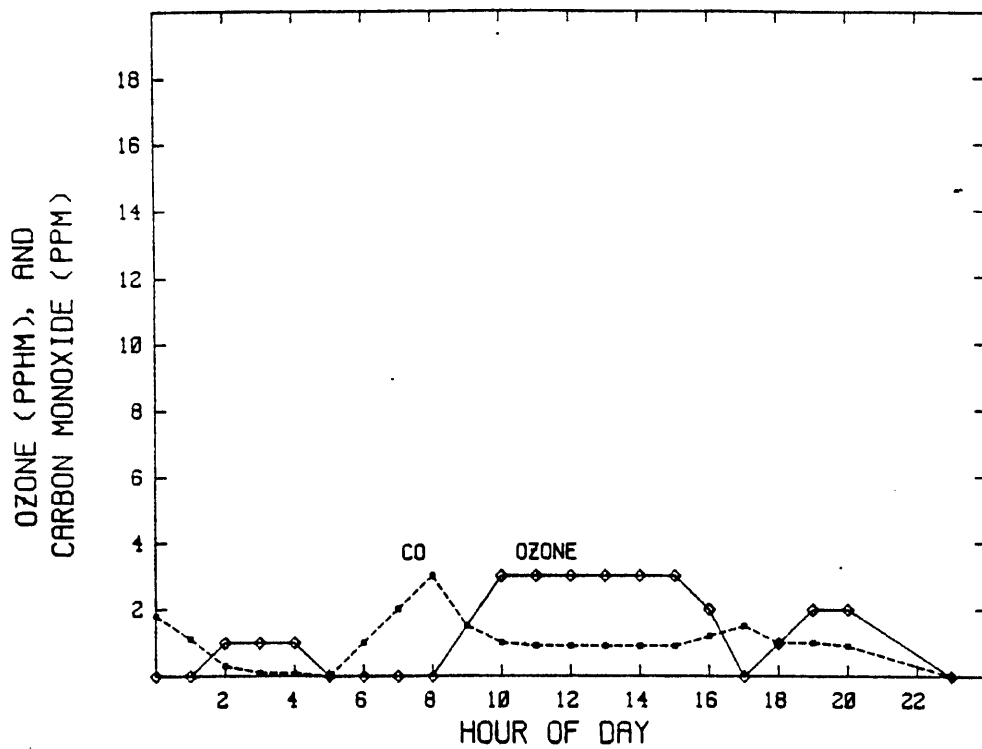
Figure 7.3-2. Carbon Monoxide, Ozone and Formaldehyde Concentrations
Measured at the South Coast Air Quality Management
District's Pico-Rivera Monitoring Station, 19 January 1983.
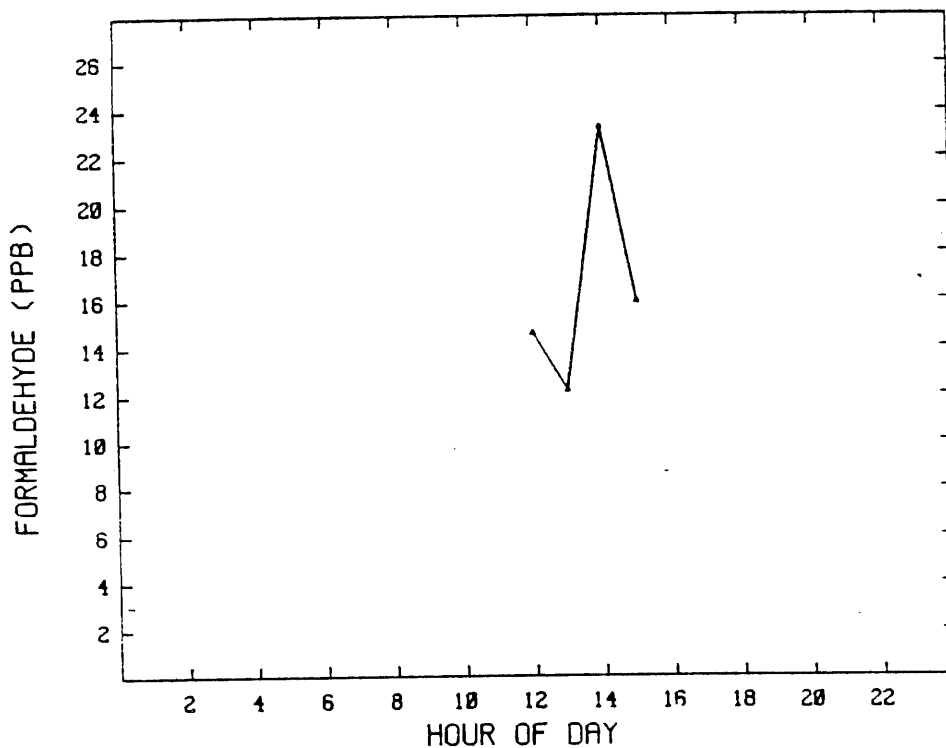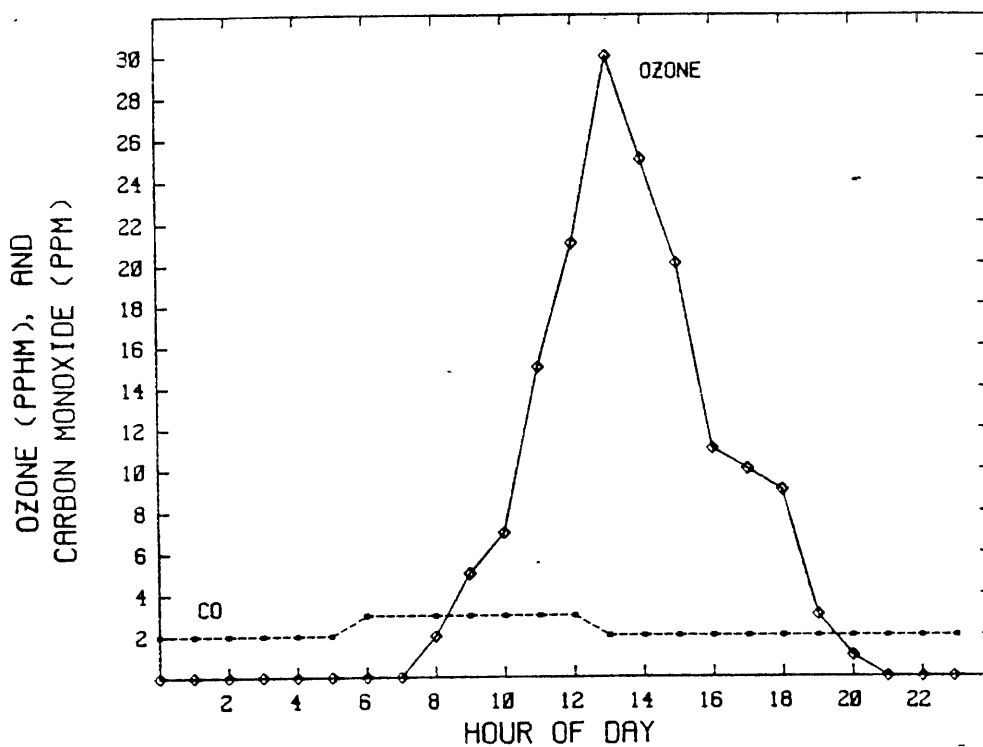
Figure 7.3-3. Carbon Monoxide, Ozone and Formaldehyde Concentrations Measured at the South Coast Air Quality Management District's Azusa Monitoring Station, 14 June 1983.

concentrations with time at Lennox, Pico-Rivera and Azusa, respectively. Several time series analyses were performed, but none resulted in a statistically significant correlation.

A multiple linear regression analysis of the entire data set yielded the following equation:

$$HCHO = 1.11 \ [CO] + 13.1 \ [O_3] + 7.19 \qquad (7.3\text{-}3)$$

The correlation coefficient for this equation was 0.383, indicating a rather poor fit. Regression analyses were also performed on the data corresponding to each monitoring station. The equation having the highest correlation was that for the Pico-Rivera station (winter and summer data combined):

$$HCHO = 1.92 \ [CO] + 12.1 \ [O_3] + 3.92 \qquad (7.3\text{-}4)$$

In this case, the correlation coefficient was 0.662. Figure 7.3-4 compares the measured HCHO values with those predicted by Equation 7.3-4. The straight line represents a perfect fit. Considerable scatter is apparent.

The results of these analyses of the data from this measurement program provide no reason to depart from the conclusion stated in the previous section, i.e. that predictive equations derived from data for one geographic area are not generalizable to other areas of the State.

7.4   REFERENCES

Dixon, W.J. and F.J. Massey, Jr. 1969. Introduction to statistical analysis, Third Edition. McGraw-Hill Book Company, New York, NY.

Grosjean, D. 1982. "Formaldehyde and other carbonyls in Los Angeles air," Environmental Science and Technology 16(5):254-262.

Grosjean, D., R.D. Swanson, and C. Ellis. 1983. "Carbonyls in Los Angeles air: Contribution of direct emissions and photochemistry," Science of the Total Environment 29:65-85.

Hanst P.L., N.W. Wong and J. Bragin. 1982. "A long-path infrared study of Los Angeles smog," Atmospheric Environment 16:969-981.
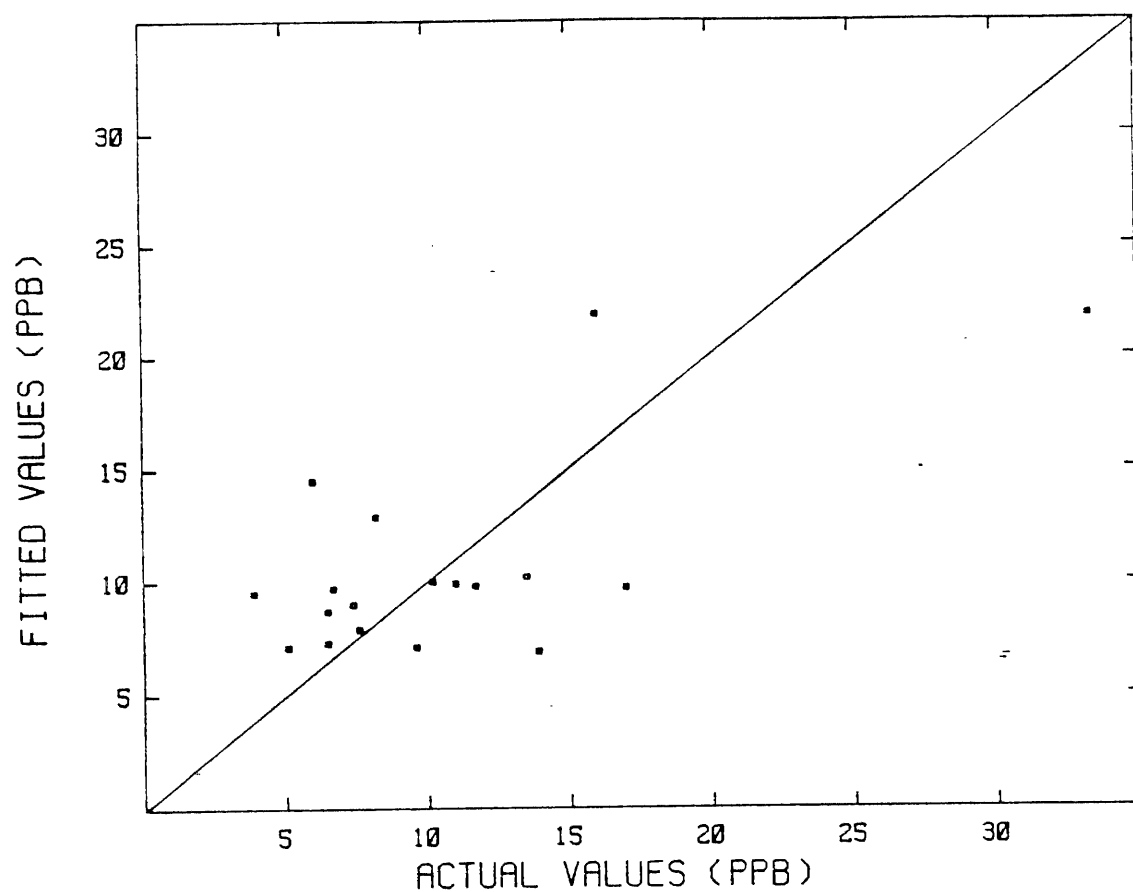
Figure 7.3-4.   Comparison of Formaldehyde Concentrations Measured at
Pico-Rivera Monitoring Station With Values Predicted
by Multiple Linear Regression Equation. (Diagonal Line
Represents Theoretical Perfect Fit.)

Hoggan, M., A. Davidson and D.C. Shikiya. (Undated). Seasonal and diurnal variation in air quality in California's South Coast Air Basin. South Coast Air Quality Management District, El Monte, CA.

Tuazon, E.C., A.M. Winer, R.A. Graham and J.N. Pitts Jr. 1980. Advances in Environmental Science and Technology 10:259.

ESTIMATION OF PUBLIC EXPOSURE TO FORMALDEHYDE

California citizens are exposed to formaldehyde and other aldehydes in five major environments. First, they are exposed to ambient formaldehyde whenever they are outdoors. In addition, a rather small portion of indoor exposure is due to infiltration of formaldehyde-laden outdoor air. "Hot spot" exposure results from proximity to major emission sources of formaldehyde. Residential exposure is due primarily to outgassing of formaldehyde from construction materials, and to indoor combustion sources. Transit exposures occur primarily as a result of motor vehicle emissions. Finally, workers in industries that use formaldehyde-based substances such as urea-formaldehyde resin may be exposed to significant levels of this chemical.

The purpose of the analysis described in this chapter was to obtain an estimate of the typical California citizen's time-weighted average exposure to formaldehyde. The method, which is presented in Section 8.1, is based upon a probabilistic simulation model. Results of the analysis are presented and discussed in Section 8.2.

8.1   METHODOLOGY

8.1.1   Simulation Methods

The objective of our analysis was to estimate the time-weighted average (TWA) exposure of a typical California resident to formaldehyde. The TWA is defined as:

$$TWA = \frac{\sum_i C_i T_i}{\sum_i T_i} \qquad (8.1\text{-}1)$$

where C_i and T_i are the formaldehyde concentration and time spent, respectively, in exposure environment i. To simplify the calculation, we let the T_i represent time fractions, so that they sum to one. Since our field sampling

showed no difference between residential and the few workplace exposures measured, the two categories were combined into one: "indoors." Given the paucity of our data, and the existence of high-formaldehyde exposures in certain occupations, it is possible that this assumption may result in an underestimate of actual exposure. Occupational exposures, however, were outside the scope of this study. "Hot spot" exposure were excluded from the exposure model because (1) with one exception, our field studies showed no significant increase in ambient formaldehyde concentrations downwind from suspected point sources and (2) few people live near these facilities.

Since ambient and indoor formaldehyde concentrations vary from hour to hour and from place to place, and since people vary widely in their activities, there can be no single value for the time-weighted average exposure. The basis of our approach was the assumption that both C_i and T_i are random variables having probability distributions which can be approximated from field and literature data. We used a "crude Monte Carlo technique" (Hillier and Lieberman, 1974) to generate TWA estimates from these distributions. Figure 8.1-1 shows an example of the Monte Carlo technique. First a cumulative probability distribution is constructed from measurement data. Then, using a random-number table or computer program, a random number between 0 and 1 is selected. In the example, this number is 0.5269, which is the probability that the value of the random variable X is less than or equal to the value displayed on the x axis.

Figure 8.1-2 shows the simulation model used to estimate public exposure to formaldehyde. The three exposure environments were "indoor" (i = 1), commuting (i = 2) and outdoors (i = 3). To simplify the analysis, the fraction of time spent indoors (T_1) was assumed to be constant. Therefore the sum of the time spent commuting and outdoors would be $1 - T_1$. In the model, T_2 is a random variable, so that $T_3 = 1 - T_1 - T_2$. The probability distributions for T_2 and C_1 through C_3 are discussed in the next section. Note that separate concentration distributions were used for mobile home, non-mobile homes less than four years old, and all other non-mobile homes. Each "box" in Figure 8.1-2 represents selection from a time or concentration distribution. As shown in Equation 8.1-1, the appropriate pairs of concentrations and times are multiplied; all these products are then summed.
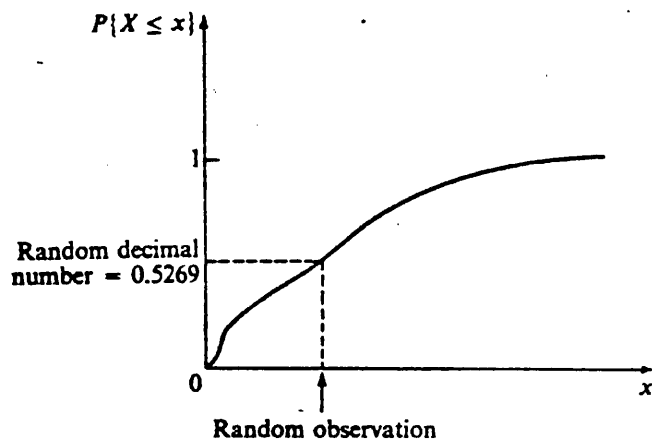
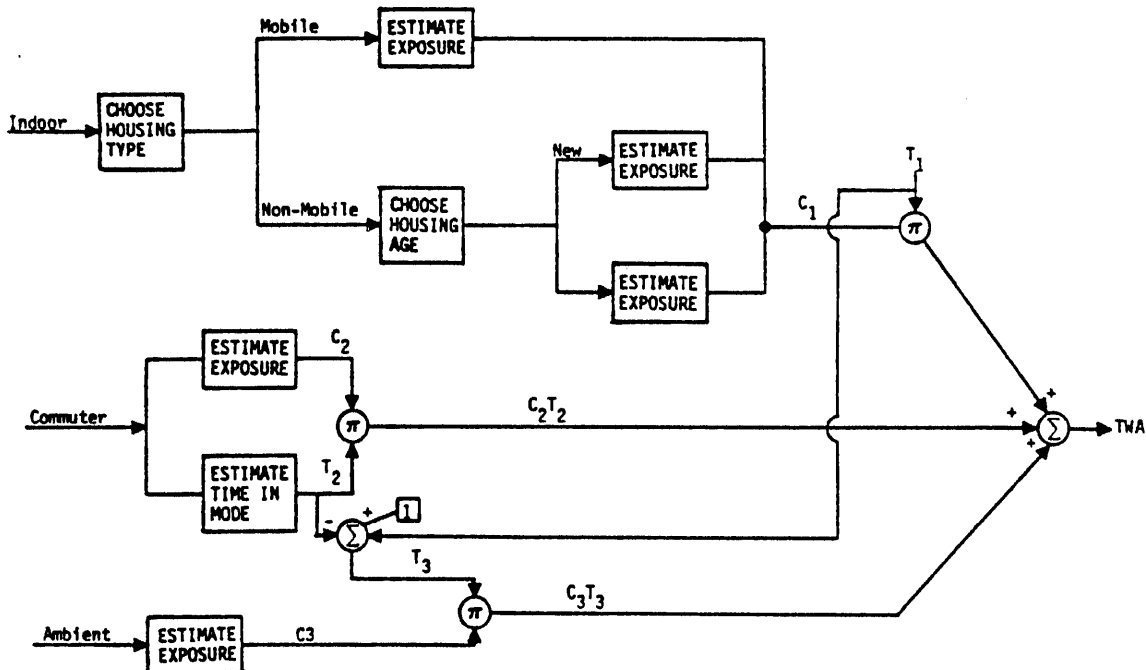Figure 8.1-1. Example of the Monte Carlo Sampling Technique.

Figure 8.1-2. Schematic of the Monte Carlo Model Used For Estimating Total Time-Weighted Average Formaldehyde Exposure.

8.1.2   Model Inputs

8.1.2.1   Time Spent in Exposure Environments

As was discussed in Section 3.2.3, people spend the great majority of their time indoors. Research summaries presented by the National Research Council (1981) indicate that the indoor fraction is about 0.90; this value was used in our model. The same source gives 3 to 5 percent for the time spent "in transit." According to an analysis by the California Department of Transportation (Lobb and Chen, 1979), the average home-work (round trip) time fraction in the South Coast Air Basin ranges from 0.026 to 0.034. A survey cited by the National Research Council indicated commuting time fractions of up to 0.069 (100 minutes per day) for U.S. cities. Table 8.1-1 shows the commute time frequency distribution used in our model. Finally, the outdoor exposure fraction was computed to be 1 minus the sum of the indoor and commuter fractions.

8.1.2.2   Exposure Distribution

A cumulative distribution of ambient formaldehyde concentrations was obtained by combining the four-study data set described in Section 7.3.1 with our winter and summer monitoring station data. Since most of these measurements were made during smog episodes, the distribution may be skewed toward higher values than those which would be obtained were year-round sampling results available. However, since ambient exposure is weighted quite lightly in our model, even substantial errors would not affect the ultimate predictions severely. Figure 8.1-3 shows the ambient HCHO distribution.

Separate distributions were constructed for non-mobile homes over four years old, non-mobile homes under four years old, and mobile homes. These are denoted by A, B, and C, respectively, in Figure 8.1-4. All three distributions are based upon our passive sampler monitoring results. The probabilities of choosing a mobile home and a non-mobile newer home were 0.0364 and 0.1364, respectively; these values were based upon 1980 U.S. Census data (USDOC, 1983). Finally, the commuter exposure distribution, which was also based upon our field data, is shown in Table 8.1-2.

Table 8.1-1
CUMULATIVE DISTRIBUTION OF PERCENT OF TIME
SPENT IN COMMUTING ENVIRONMENT

Minutes per Day[a]	Percent of Day Spent Commuting	Cumulative Percent of People
1-10	0.76	9.0
11-20	2.15	41.4
21-30	3.54	60.1
31-40	4.93	84.1
41-50[b]	6.32	100.0

[a] These data are from the California Department of Transportation (Lobb and Chen, 1979). Midpoints were used to represent commuting times.
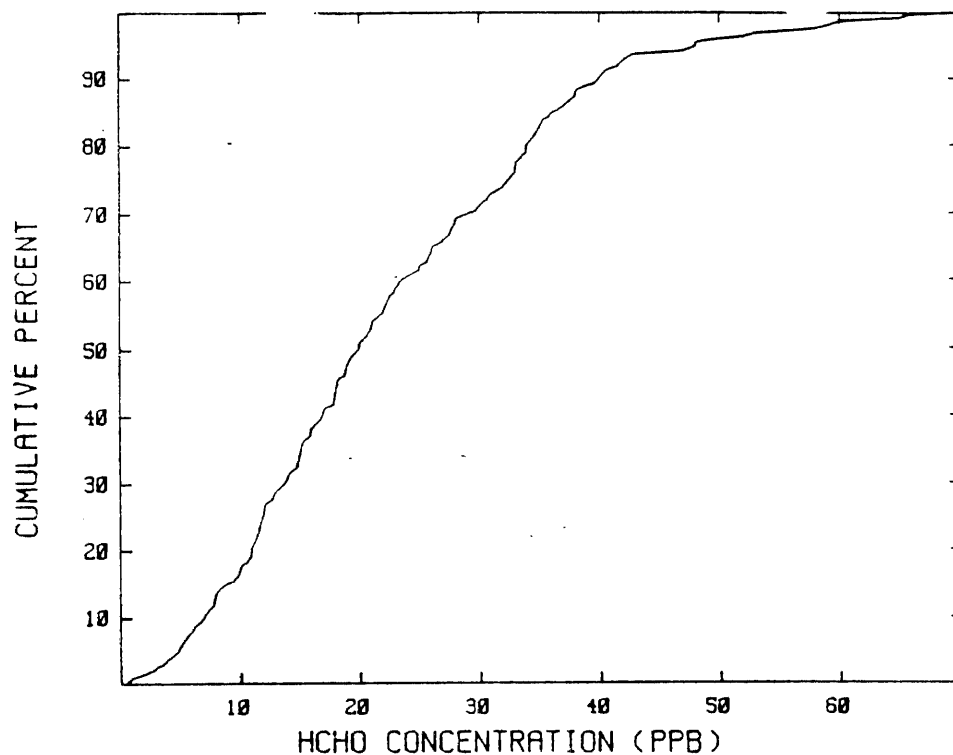
[b] Upper bound of 50 taken from NRC (1981); see text.

Figure 8.1-3. Cumulative Distribution of Ambient Formaldehyde Concentrations
Used in Monte Carlo Simulation of Public Exposure.
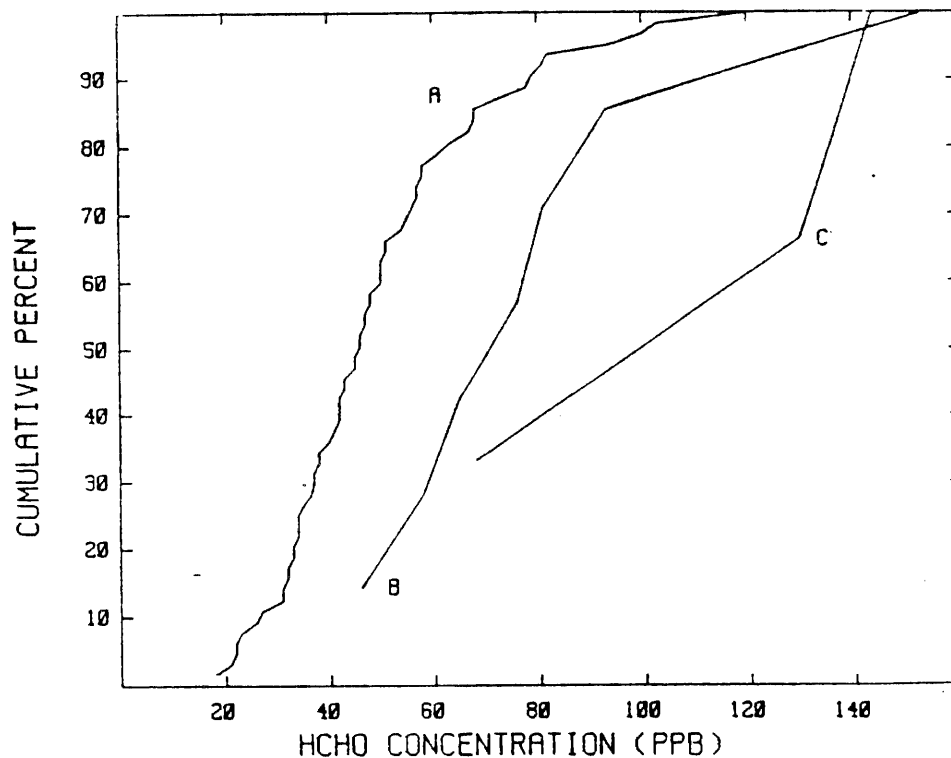
Figure 8.1-4. Cumulative Distribution of Indoor Formaldehyde Concentrations
in (A) Non-Mobile Homes Over Four Years Old, (B) Non-Mobile
Homes Four Years Old or Under, and (C) Mobile Homes.

Table 8.1-2

CUMULATIVE DISTRIBUTION OF COMMUTER EXPOSURES

Formaldehyde Concentration (ppb)	Cumulative Fraction
10.7	7.69
11.3	15.38
12.9	23.08
21.1	30.77
22.5	38.46
22.9	46.15
27.3	53.85
30.5	61.54
31.1	69.23
37.4	76.92
39.4	84.62
48.4	92.31
91.5	100.00

8.2   EXPOSURE ESTIMATE

The Monte Carlo simulation program was written in BASIC and run on an Apple II Plus computer. One thousand random exposure cases were simulated. Since a different random number was generated for each of the distributions from which samples were drawn, no single trial was biased toward all high or low exposure values.

Figure 8.2-1 shows the frequency distribution of time-weighted average formaldehyde exposures predicted by the model's 1000 trials. The irregularity of the frequency distribution curve is due to the fact that relatively few concentration values were available to be chosen. The mean and median HCHO exposures for this run were 53 and 46 ppb, respectively. Another 1000-trial run, in which the time spent indoors was decreased to 85 percent and the time commuting was assumed to range between 4 and 8 percent, resulted in a mean of 51 ppb.

The cumulative frequency distribution for the first model run is shown in Figure 8.2-2. Comparison of this curve with Curve A (older non-mobile homes) in Figure 8.1-4 shows the overwhelming influence of indoor exposure on the time-weighted exposure. The medians are almost identical, and the higher mean for the time-weighted average curve is due mainly to inclusion of the new non-mobile homes and mobile homes in the sample. The highest predicted exposure was 143 ppb, and 95 percent of the population would be exposed to 107 ppb or less.

Although an assessment of health effects was outside the scope of this project, some comparison of our exposure modeling results with known response thresholds is necessary for placing our findings in perspective. According to data compiled by the National Research Council (1981b), the threshold for eye irritation is about 50 to 500 ppb, although sensitive individuals may perceive discomfort at concentrations of 20 ppb. Upper airway irritation begins at about 100 ppb, although thresholds of 1 ppm (1000 ppb) are reported more frequently. Lower airway and pulmonary e ʿcts occur at much higher levels (5 to 30 ppm). Pulmonary edema, pneomoniti. ..d death occur at exposures exceeding 50 to 100 ppm (50,000 to 100,000 ppb). Thus
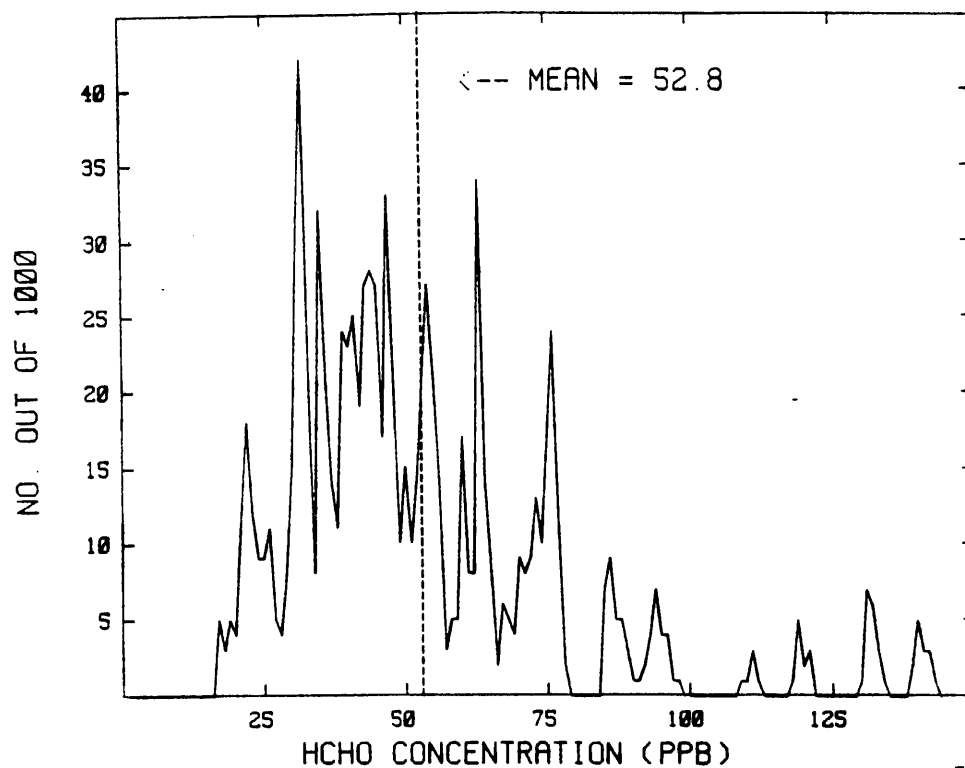
Figure 8.2-1. Monte Carlo Simulation Results: Distribution of Exposures.
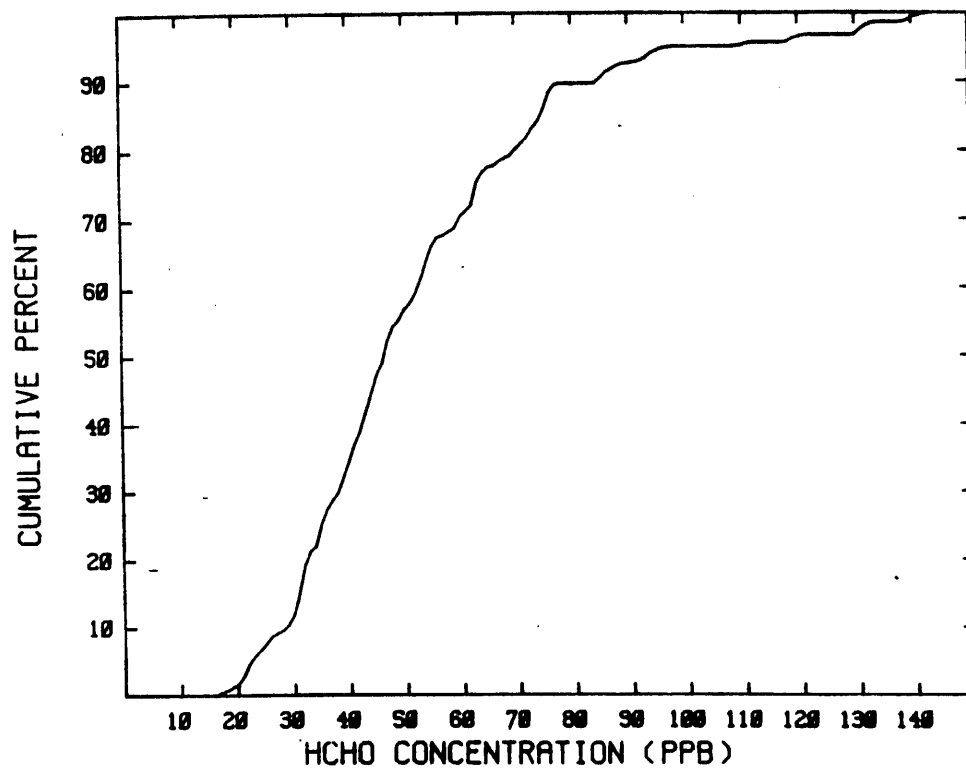

Figure 8.2-2. Monte Carlo Simulation Results: Cumulative Frequency
Distribution.

sensitive individuals could experience eye discomfort at the median level and upper airway irritation at the upper end of the range of exposures predicted by our model.

The U.S. Environmental Protection Agency (1984) has recently published information on the relative carcinogenic potency of 52 chemicals, including formaldehyde, evaluated by the Carcinogen Assessment Group (CAG). Before discussing this further, it should be noted that the findings of the CAG are based on estimates of low-dose risk using the upper 95-percent confidence limit for the linearized multistage model. These estimates are extrapolated from lifetime animal inhalation studies using average lifetime formaldehyde concentrations of from 0.4 to 2.7 ppm and the direct relevance to human exposures at the ppb level is uncertain. A measure of risk used by the CAG is the slope of the dose-response curve; for formaldehyde this value is 2.14×10^{-2} (mg/kg-day)$^{-1}$. If one assumes 70 kg body weight, 100 percent absorption of formaldehyde, and a lifetime average exposure to 1 ppb, then the dose is equal to:

$$\text{Dose} = (1 \text{ ppb})(1.226 \ \mu g/m^3/\text{ppb})(10^{-3} mg/\mu g)(20 \ m^3/\text{day})/70 \text{ kg}$$
$$= 3.50 \times 10^{-4} \text{ mg/kg-day}$$

The risk is equal to the dose times the slope:

$$\text{Risk (1 ppb)} = (3.50 \times 10^{-4})(2.14 \times 10^{-2}) = 7.49 \times 10^{-6}$$

The risk for the median exposure of 46 ppb would be 3.4×10^{-4} or about 3 in 10,000.

8.3   REFERENCES

Hillier, F.S. and G.J. Lieberman. 1974. Operations research, 2nd Edition. Holden-Day, Inc., San Francisco, pp. 628-637.

Lobb, O. and B. Chen. 1979. The 1976 urban and rural travel survey. Volume IV. Summary of findings: travel data. California Department of Transportation and Southern California Association of Governments.

National Research Council. 1981a. Indoor pollutants. National Academy Press, Washington, D.C.

National Research Council. 1981b. Formaldehyde and other aldehydes. National Academy Press, Washington, D.C.

U.S. Department of Commerce, Bureau of the Census. 1982. Supplementary report. Provisional estimates of social, economic and housing characteristics, states and selected standard metropolitan statistical areas, PHC80-S1-1.

U.S. Environmental Protection Agency. 1984. Health assessment document for inorganic arsenic, final report. Office of Health and Environmental Assessment, Environmental Criteria and Assessment Office, EPA-600/8-83-021F.

APPENDIX A

AMBIENT AIR SAMPLING PUMP CALIBRATION CURVES
AND SAMPLE CALCULATION OF FORMALDEHYDE CONCENTRATION

A.1   PUMP CALIBRATION CURVES

As described in Section 6.2.1, the rotameters associated with the MSA Model G pumps used for the impinger-based sampling of ambient formaldehyde were calibrated with a soap film flowmeter. Figures A.1-1 through A.1-3 show the calibration data for the three rotameters. A least squares linear regression line has been fitted to the data for each pump.

A.2   SAMPLE CALCULATION

As an example let us use Sample 1-1. The rotameter readings at the start and end of the run were 2.0 and 1.8 standard cubic feet per hour (scfh), respectively. From the curve for Pump No. 20/Rotameter No. 4, the actual flow rates were 1.19 and 1.10 L/min, respectively, or an average of 1.145 L/min. Since the sampling time was 60 min exactly, the sampled volume was (1.145 L/min)(60 min) = 68.7 L. The ambient air temperature was 21.5°C, and the calibration temperature was 24°C. From Equation 6.2-1, the adjusted sample volume was:

$$V_a = (68.7 \text{ L})[24 + 273)/(21.5 + 273)]^{1/2}$$
$$= 69.0 \text{ L} = 0.0690 \text{ m}^3$$

Since 0.89 µg were detected in the impinger solution (see Table 6.3-2), the adjusted concentration was 0.89 µg/0.0690 m^3 or 12.9 µg/m^3. The concentration in ppb can be obtained directly by substituting the mass, the uncorrected field volume (V_f), and field temperature (t_f) into Equation 6.2-5:

$$C_v = \frac{1.5867 \times 10^{-4} \ (0.89 \ \mu g)(21.5 + 273.15)^{1.5}}{(0.0687 \ \text{m}^3)}$$
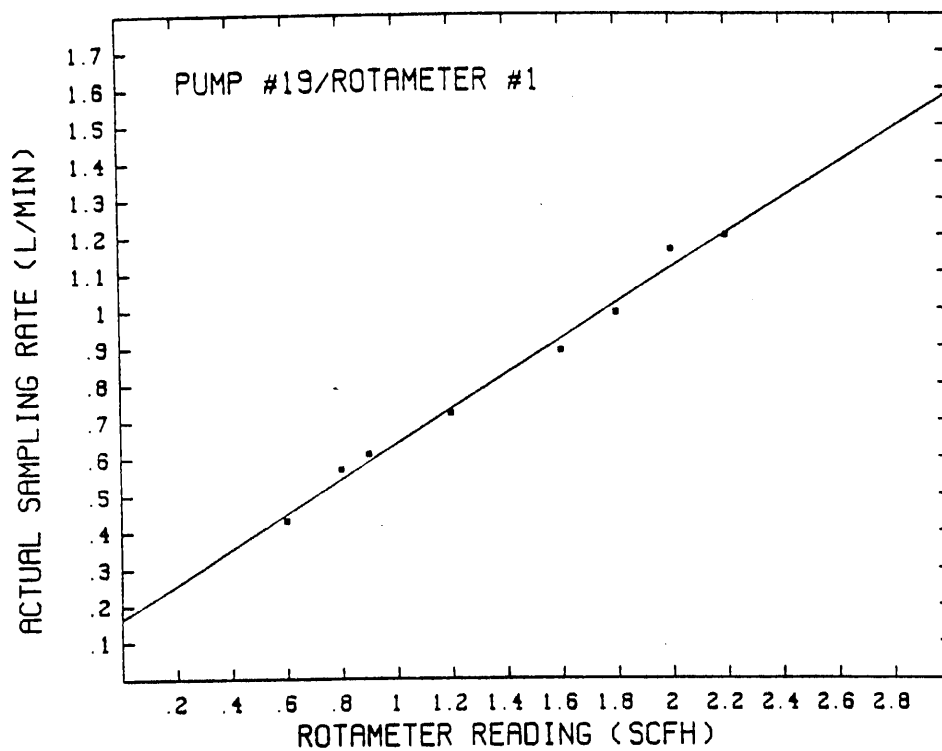
$$= 10.4 \text{ ppb}$$

Figure A.1-1.   Calibration Curve For Combination of Pump 19 and Rotameter 1.
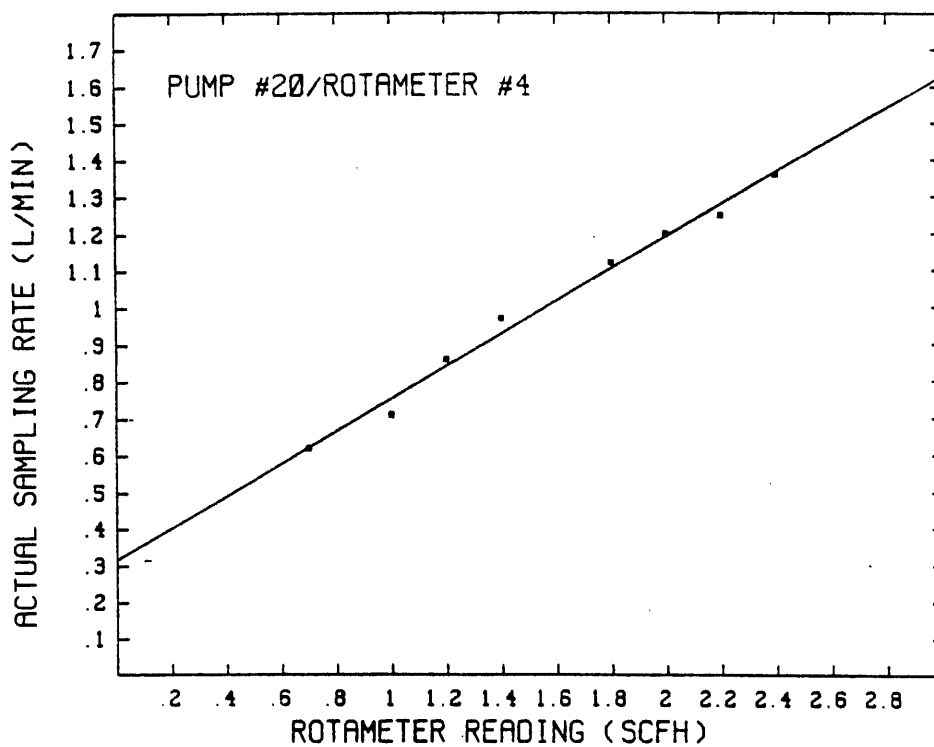

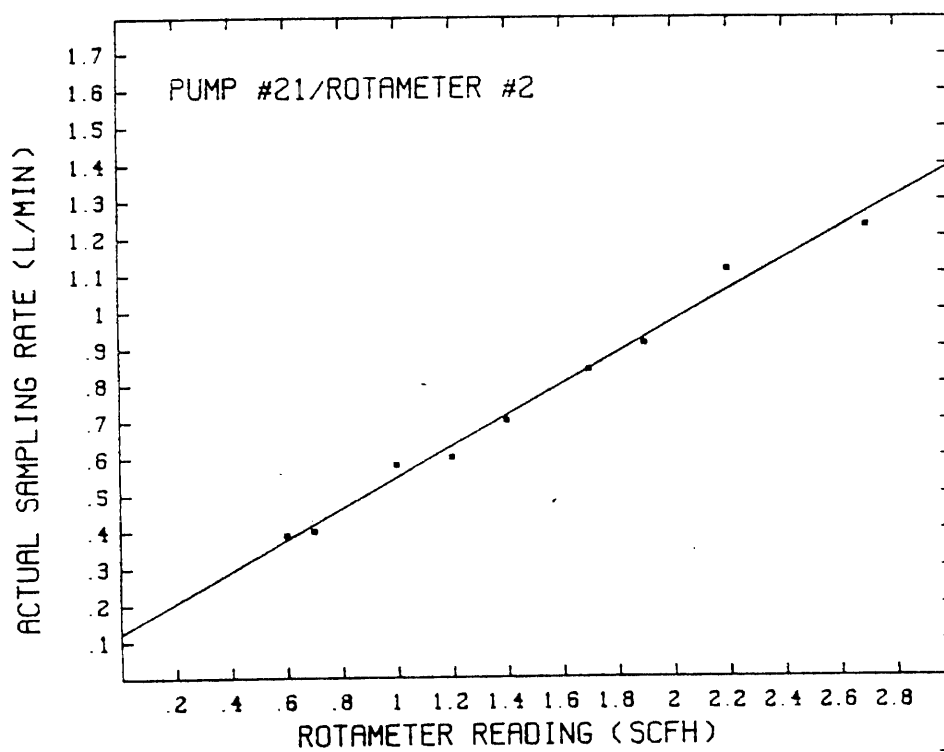Figure A.1-2.   Calibration Curve For Combination of Pump 20 and Rotameter 4.

Figure A.1-3. Calibration Curve For Combination of Pump 21 and Rotameter 2.

APPENDIX B

ENVIRONMENTAL RESEARCH AND TECHNOLOGY (ERT)
PROTOCOLS FOR SAMPLING AND ANALYZING AMBIENT
FORMALDEHYDE BY THE DNPH/HPLC METHOD

TECHNICAL INSTRUCTION

Title: SAMPLING OF CARBONYL COMPOUNDS IN AMBIENT AIR

Page 1 of 5
Number: 6000-302
Date: 6/17/81
Revision: 0

1.0 Introduction

Carbonyl compounds react rapidly with 2,4-dinitrophenylhydrazine (DNPH) in acidic media to form yellow to orange-colored hydrazones. The color depends on the nature of the carbonyl compound, and the amount of product formed is related to the quantity of the carbonyl compound presented to the reagent.

To sample for carbonyl compounds present in ambient air, air is drawn at a known flow rate through an impinger containing an acidic aqueous solution of DNPH mixed with a hydrocarbon solvent. Any carbonyl present reacts quantitatively with DNPH and therefore is scrubbed from the sampling air stream. At the completion of sampling, the sample is returned to the laboratory for isolation, separation and quantitation of the hydrazone products by high-pressure liquid chromatography. Knowing the volume of air sampled and the amount of hydrazones collected, the concentration of various carbonyl compounds in air may then be calculated.

2.0 Materials

2.1 DNPH Reagent: This is an aqueous solution containing 2.5 g of 2,4-dinitrophenylhydrazine in one liter of ∿2N hydrochloric acid. Ten milliliters of this solution are used in the impinger for sampling. The DNPH solution should be extracted with 50 ml of hexane/CH_2Cl_2 (30:70 by volume) at least five times to lower the hydrazone blank in the reagent. The DNPH solution so prepared should be analyzed by HPLC to determine if the hydrazone is acceptable.

2.2 Cyclohexane/Isooctane Mixed Solvent: This reagent is prepared from mixing ten parts (by volume) of cyclohexane to one part of isooctane. These solvents must be analyzed for carbonyl impurities before use. Purification of these solvents, if needed, is accomplished with distillation in the presence of DNPH. This reagent is used to increase the sampling efficiency of the impinger for carbonyls. For a one-hour sampling at ∿1 liter per minute, 10 ml of this solvent mixture are used in the impinger.

2.3 Distilled Deionized Water: This is for rinsing the impinger after sampling.

2.4 10 W Motor Oil: This oil is used for lubrication of the sampling pump.

2.5 Pump Filter: The sampling pump has an inlet and outlet filter. The inlet filter usually remains fairly clean for this type of operation, but nevertheless should be inspected every 200 hours of operation. The outlet filter traps oil and debris and prevents them from being introduced into the environment. This filter gets oily quickly and should be inspected every 72 hours of operation. Oil which pooled in the cannister housing the exhaust filter should be drained off. When the filter appears to be soaked with soil, it should be replaced with a new one.

2.6 Field Log Sheet: This is a form for entering all sampling information such as sampling date, sampling start and stop times, sample number, upstream and downstream gauge reading of sampling pump.

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2.7 Stopcock Grease: This is for lubrication of the impinger side-arm to facilitate connection and removal of the Latex tubing. Do not use for lubrication of the ground glass joint of the impinger.

3.0 Apparatus

3.1 Midget Impinger: This apparatus consists of two parts: the bottle, of ∿30 ml, to contain the reagent for sampling, and the jet to bubble air through the reagent. The two parts are fitted together via a ground glass joint.

3.2 Wash Bottle: A polyethylene bottle to contain distilled deionized water for rinsing of impingers after sampling.

3.3 Sampling Pump: A Gast vacuum pump - fitted with a critical orifice to limit the flow to ∿1 L/min. Oil must be present in the oil jar of the pump during operation. Peridically, the critical orifice should be checked for clogging by sighting against a light source. The orifice may be flushed with alcohol for cleaning.

3.4 Latex Tubing: The tubing is to connect the impinger to the sampling pump so that air can be drawn through the impinger.

3.5 Culture Tube with Screw Cap: Each tube contains the reagents needed for one sampling. It is labeled with a sample number. The reagents are transferred to the impinger for sampling, after which they are transferred back to the culture tube for shipping to the laboratory.

3.6 Tripod Stand with Clamp: They are for supporting the impinger during sampling.

4.0 Method

4.1 Clamp the impinger bottle to the tripod stand.

4.2 Uncap a culture tube and transfer the sampling reagents into the impinger bottle. Immediately recap the empty tube and set it aside. Avoid contaminating the tube and cap with foreign matter.

4.3 Place the impinger jet into the bottle and let the ground glass joint come into contact. Forcing the joint together may cause freezing of the joint, making the parts difficult to separate. No grease or lubricant should be used with the joint, as it may contaminate the sample.

4.4 Wipe a thin film of stockcock grease on the side-arm of the impinger. Avoid excessive greasing.

4.5 Connect one end of the Latex tubing to the side-arm of the impinger and the other end to the inlet of the Gast sampling pump.

4.6 Enter Sample Number, Sampling Date, and Sampling Start Time in the Field Log Sheet.

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4.7 Apply power to the pump to initiate sampling. No violent bumping should occur inside the impinger. Otherwise, sampling flow rate may be too high indicating the orifice may have been broken off. On the other hand, if hardly any air flow is observed, the orifice may have been clogged or the ground glass joint is not in contact. In either case, sampling should be stopped and the cause be investigated. If trouble persists, the sample should be voided.

4.8 When sampling is in progress, observe the readings of the vacuum gauges upstream (air flowing into) and downstream (air flowing away from) of the orifice. The upstream gauge should show fewer than 5 in. Hg and the downstream gauge should read ∿23 in. Hg. Should the upstream gauge show a higher reading, obstruction to the sampling flow anywhere between the impinger jet and the point just ahead of the orifice is indicated. If the downstream gauge shows a low reading, the pump is not drawing a good vacuum, indicating a potential problem with the pump at leakage downstream of the orifice. Previous gauge readings would indicate if the pump is wearing down with time.

4.9 Enter the Upstream and Downstream Gauge Readings into the Field Log Sheet.

4.10 Upon completion of sampling, stop the Gast pump. Enter the Stop Time into the Field Log Sheet.

4.11 Remove the Latex tubing from the side-arm and uncouple the impinger jet from the bottle. Let the jet touch the inside wall of the bottle just above the solution. Allow the liquid inside the jet to drain completely. Then remove the jet.

4.12 Transfer the solution of the impinger bottle back to the original culture tube used for shipping. Avoid any spills. If so, note in the Remarks column of the Field Log Sheet for that sample.

4.13 With the wash bottle, rinse the impinger bottle with about 5-10 ml of distilled deionized water. Do not use more than 10 ml of water. Transfer all washes to the culture tube.

4.14 Cap the culture tube tightly and mark the label with an S to indicate the content has been used for sampling and to avoid mixed-up with fresh samples. Put the sample in cold storage and package it properly to avoid breakage during shipping. For shipping, the samples should be placed in a stryrofoam container with dry ice to maintain the samples cold during shipping. Special carrier should be used for quick delivery.

4.15 After sampling all samples and the corresponding data, log sheets are to be returned as soon as possible, but no later than three days, to the laboratory. The address is:

   ENVIRONMENTAL RESEARCH & TECHNOLOGY, INC.
   2625 Townsgate Road, Suite 360
   Westlake Village, California 91361

   Attention: Laboratory Supervisor

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4.16 Sample blanks: Sample blanks are used to assess the hydrazone levels in the reagent after the process of handling, shipping to and from the field. A sample blank is obtained by transferring the DNPH sampling reagent from the test tube to the impinger and then immediately back to the test tube. In n samples are to be collected in a day, then the number of sample blanks should be equal to n or three, whichever is larger. Return sample blanks with each set of samples. Each blank should be clearly marked and entered into the log sheet with the samples.

4.17 DNPH sampling reagent stored refrigerated are good for three weeks. Discard unused reagents if they are three weeks old.

ERT CARBONYL SAMPLING FIELD LOG SHEET

SAMPLE NO.	DATE	SAMPLING TIME		GAUGE READING		REMARKS:
		START	STOP	UPSTREAM	DOWN-STREAM	

EXCERPT FROM
TECHNICAL INSTRUCTION - SAMPLING OF CARBONYL COMPOUNDS IN AMBIENT AIR
(6000-302)

1. Clamp the culture tube with absorbing reagent to the ring stand.

2. Uncap the labelled culture tube containing DNPH reagent and organic
    (clear) reagent. Avoid contaminating the caps with foreign matter
    by placing the cap in a protective plastic bag or covered jar.

3. Place the Teflon impinger head into the tube and place a disposable
    pipette tube in the center of the impinger head. Adjust the inlet
    tube till the tip is approximately 1/8 inch off the bottom of the
    reagent tube then tighten the knurled nut and o-ring around the
    inlet tube gently.

4. Connect one end of the Latex tubing to the side-arm of the impinger
    and the other end to the inlet of the Gast sampling pump.

5. Enter Site, Sample Number (from DNPH culture tube), Sampling Date,
    and Sampling Start Time in the Field Log Sheet.

6. Insure that the downstream gauge valve and the outlet gauge valve
    are completely closed. Also check the oil level of the pump's oil
    jar. Apply power to the pump to initiate sampling. No violent
    bubbling should occur inside the impinger. Otherwise, sampling flow
    rate may be too high indicating the orifice may have been broken
    off. On the other hand, if hardly any air flow is observed, the
    orifice may have been clogged or the ground glass joint is not in
    contact. In either case, sampling should be stopped and the cause
    investigated. If trouble persists, the sampling should be voided.

7. When sampling is in progress, record the reading of the vacuum gauge
    downstream of (air flowing away from) the orifice. The upstream
    gauge should show 0.0 in. Hg and the downstream gauge should read
    20-26 in. Hg. If the downstream gauge shows a low reading, the pump
    is not drawing a good vacuum indicating a potential problem with the
    pump at leakage downstream of the orifice. Previous gauge readings
    will indicate if the pump is wearing down with time.

8. Enter the Downstream Gauge Readings into the Field Log Sheet.

9. Upon completion of sampling, stop the Gast pump. Enter the Stop
    Time and Gauge reading into the Field Log Sheet. Remove the tubing
    from the impinger's side arm. Loosen the disposable inlet tube and
    raise the tip above the liquid level. Blow out any reagent in the
    tube then remove and discard the tube. Remove impinger head from
    reagent tube. Cap gauge tube and remove from the tripod stand.

10. Label the sample tube with date. Put the sample in cold storage and
    package it properly to avoid breakage during transport. For
    transport, the samples should be placed in a styrofoam container
    with dry ice to maintain the samples cold.

11. Return all samples, the corresponding data and log sheets as soon as possible to the laboratory. The address is:

> ENVIRONMENTAL RESEARCH & TECHNOLOGY, INC.
> Attention: Laboratory Supervisor
> 2625 Townsgate Road, Suite 360
> Westlake Village, California 91361

12. Sample Blanks: Sample blanks are used to assess the hydrazone levels in the reagent after the process of handling, shipping to and from the field. Unexposed sample reagent should be returned to the laboratory to be analyzed as field blanks. Two blanks should be submitted with each twelve samples. Each blank tube should be clearly marked BLANK, dated, and entered into the log sheet with the samples.

COMPARISON OF NEW SAMPLING HEAD AND IMPINGER, 4/5/83

As part of a series of control experiments carried out at the ERT environmental chamber facility, two carbonyl samples were collected side by side, one using a microimpinger and the other using a culture tube and the new sampling head.

The matrix air contained in a 4 m^3 chamber constructed from transparent Teflon film, included ozone (140 ppb), acetaldehyde (150 ppb) and formaldehyde (20 ppb). The chamber was covered with opaque plastic film so that no acetaldehyde or formaldehyde was lost due to photolysis. The chamber temperature was ~25°C, and the matrix air (purified air containing less than 10 ppb of oxides of nitrogen and no detectable amounts of sulfur dioxide or ozone) was dry, i.e., the measured dew point was -16°C.

The two samples were collected in parallel, starting at 16:15 PDT for 30 minutes. Flow rates from calibrated sampling pumps were 0.961 L/min (impinger) and 0.940 L/min (tube with new sampling head). Both sampling devices contained 10 mL of the same reagent, aqueous DNPH and organic solvent.

Results were as follows:

	Formaldehyde		Acetaldehyde	
	µg/sample	ppb	µg/sample	ppb
New sampling head	0.84	23.8	9.24	180
Impinger	0.66	18.2	8.17	156
Average		±2.8		±12

Conclusions:

-- Measured concentrations were in good agreement with the nominal concentrations (calculated from the amount injected and the chamber volume, with an uncertainty of ~10-15%).

-- Agreement between the two sampling devices is satisfactory, 13% for formaldehyde and 7% for acetaldehyde.

-- The higher values obtained with the new sampling head may indicate better collection efficiency due to improved mixing during sampling and/or less opportunities for sample loss since the use of the tube with the new sampling head involves fewer transfer steps. This may be verified by carrying out additional side-by-side comparisons.

Title:

ANALYSIS FOR CARBONYL COMPOUNDS IN AMBIENT AIR

1.0 INTRODUCTION

Carbonyl compounds react rapidly with 2,4-dinitrophenylhydrazine (DNPH) in acidic media to form yellow to orange-colored hydrazones. The color depends on the nature of the carbonyl compound, and the amount of product formed is related to the quantity of the carbonyl compound presented to the reagent.

Samples are collected in culture tubes with a Teflon impinger head and disposable inlet tubes according to the Technical Instruction 6000-302, Sampling of Carbonyl Compounds in Ambient Air. Analysis is achieved with HPLC after extracting the carbonyl DNPH derivatives from the sample.

2.0 MATERIALS

2.1 DNPH Reagent.

This is an aqueous solution containing 2.5 g of 2,4-dinitrophenylhydrazine in one liter of ~2 N hydrochloric acid. Ten milliliters of this solution are used in the impinger for sampling. The DNPH solution should be extracted with 50 ml of hexane/CH_2Cl_2 (30:70 by volume) at least five times to lower the hydrazone blank in the reagent. The DNPH solution so prepared should be analyzed by HPLC to determine if the hydrazone is acceptable.

2.2 Methylene chloride: hexane (30:70) extraction solvent.

This reagent is prepared from Burdick & Jackson reagents and is analyzed for impurities. Mix 150 ml CH_2Cl_2 and 350 ml C_6H_{14}.

2.3 Hydrazone standards.

The stock standard solutions are prepared by weighing 10 to 20 mg of one or several DNPH derivatives of the compounds of interest (generally C_1 to C_4 carbonyls), dissolving in methanol and bringing to 250 ml volume. The working standard is prepared when needed by diluting 15 ml stock standard to 50 ml with methanol.

3.0 EQUIPMENT

An Altex Model 332 HPLC is used to separate and detect the carbonyls. The column is an ultrasphere ODS 15 cm x 4.67 cm. The solvent is 55% acetonitrile in water. The spectrophotometer is set at 365 μm, 0.1 absorbance full scale.

Title:

ANALYSIS FOR CARBONYL COMPOUNDS IN AMBIENT AIR

4.0 ANALYSIS

Samples are received in culture tubes, chilled. The samples are refrigerated until they are analyzed.

4.1 Removal of Organic Layer

4.1.1   Draw off any of the upper cyclohexane/isooctane solvent layer using a disposable Pasteur pipette and transfer to a 10-ml disposable culture tube labelled with the sample number. Place culture tube in an aluminum block test tube holder.

4.1.2   Put one or·two Teflon/Halon boiling stones into the culture tube containing the solvent layer.

4.1.3   Cover the culture tube containing the clear solvent layer with a piece of aluminum foil about 1 to 1-1/2" square. Pierce the foil leaving a small hole for vapors to escape.

4.1.4   Place the aluminum block tube holder containing the culture tubes into a vacuum dessicator at 22 inches of vacuum and heat at 60-80°C for approximately three hours.

4.2 Extraction

4.2.1   Add 10 ml of deionized distilled water to the DNPH in each culture tube.

4.2.2   Prepare a series of four standards and three blanks to be analyzed with the samples.

4.2.3   Dilute stock standard solutions containing the hydrazones of the carbonyls expected and add aliquots of the working standard to reagent blanks.

4.2.4   Add 200 µl of an internal standard (such as cyclohexanone) to each culture tube.

4.2.5   Add 5 ml of a 70:30 hexane:methylene chloride extracting solution to each sample, standard and blank reagent in culture tubes. Cap tightly. Ensure that the cap does not leak by inverting the mixture once and checking the cap.

4.2.6   Place the culture tubes in a test tube holder.

4.2.7   Place test tube holder in a mechanical shaker. Secure the tubes and shake for 30 minutes.

4.2.8   Remove the aluminum block containing the now dried organic layer from the heated vacuum dessicator. If some liquid is still present in the tubes, return them to the dessicator until they are completely dried. Cool the tubes.

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ANALYSIS FOR CARBONYL COMPOUNDS IN AMBIENT AIR

4.2.9   Remove the sample culture tubes from the shaker and let the samples settle for 15 minutes or centrifuge them, if needed, to separate the organic and aqueous layers.

4.2.10   Remove the organic extraction layer from the culture tube using a clear disposable Pasteur pipette and put the organic extract in the small disposable culture tube containing the dried organic solvent layer with the same sample number.

4.2.11   Return the disposable culture tubes, covered with aluminum foil (with a hole in it), to the cold vacuum dessicator. Set the heat on low and heat approximately three hours at 30 to 40°C and 22 inches of vacuum.

4.2.12   Remove the culture tubes from the heated vacuum dessicator when they are completely dried. The dried samples are ready for analysis.

4.3 Analysis by HPLC

4.3.1   The samples should be analyzed using a 55% solution of acetonitrile in deionized distilled water at a flow rate of 1.5 ml/min.

4.3.2   Add 0.5 ml of methanol to the culture tube containing the carbonyl residue.

4.3.3   Dissolve residue in methanol by shaking culture tube vigorously for 10 seconds using a hand-operated test tube shaker.

4.3.4   Purge the HPLC sample loop with approximately 2 ml of methanol.

4.3.5   Clean a 50-μl syringe twice using methanol, then purge the syringe twice with sample.

4.3.6   Using the sample syringe, purge the HPLC sample loop two times with the sample to be analyzed. Be certain no bubbles get into the sample loop on the third injection as the bubbles will cause an inaccurate analysis.

4.3.7   Pull the valve handle to the "inject" position and flip the "start" toggle switch to begin analysis.

4.3.8   Push the "stop" button on the integrator to end the analysis.

4.3.9   Push valve handle to the "load" position and repeat steps (1) to the above step.

SUMMARY OF ERT CARBONYL METHOD VALIDATION STUDIES

Method Component	Results	Reference
Analytical recoveries	91-100%	(1)
Analytical detection limits	1-5 nanograms	(1)
Reproducibility of retention times	6% absolute	(1)
	$\leq$3% with internal standard	(1)
Reproducibility of concentrations	~3% stock solutions	(1)
	~6% synthetic mixtures	(1)
	~5-10% field samples	(1)
Collection efficiency of impingers:		
Formaldehyde, DNPH	92 $\pm$ 12% dry air	(2)
	99 $\pm$ 13% humid air	(2)
Formaldehyde, DNPH	111 $\pm$ 18% dry air	(2)
+ organic solvent	101 $\pm$ 27% humid air	(2)
Recovery from spiked impingers:		
Formaldehyde, DNPH	96%	(1)
Formaldehyde, DNPH	90%	(2)
+ organic solvent		
Effect of other aldehydes on collection efficiency (CE)	None	(2)
Recovery from spiked impingers after exposure to ambient photochemically polluted air	100 $\pm$ 10%	(3)
Application to ambient <u>gas-phase</u> measurements	Formaldehyde, acetaldehyde, propanal, n-butanal, methyl ethyl ketone, benzaldehyde	(3)
Application to ambient <u>particulate-phase</u> measurements	Same as above, aerosol/gas ratios $\leq 10^{-2}$	(3)

References:

(1) K. Fung and D. Grosjean, Anal. Chem., 53, 1981, 168-171.
(2) D. Grosjean and K. FUng, Anal. Chem., 54, 1982, 1221-1224.
(3) D. Grosjean, Environ. Sci. Technol., 16, 1982, 254-262.

VALIDATION OF A PASSIVE SAMPLER FOR DETERMINING FORMALDEHYDE
IN RESIDENTIAL INDOOR AIR

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ABSTRACT

A passive sampling device based on the principle of diffusion has been developed specifically for the determination of formaldehyde in residential indoor air. The device, which is inexpensive and easy to use, is capable of measuring one-week time-weighted average concentrations of formaldehyde from as low as 0.018 ppm to over 1 ppm. The sampler was validated by a series of laboratory experiments and a field study conducted in occupied residences and an office. The parameters evaluated in the laboratory and field experiments were: sampling rate; sampling period; detection limit; relative humidity effects; chemical interferences; shelf life; sample stability; overall precision; bias; and overall accuracy. The performance of the passive sampler compared favorably to that of a reference pump/bubbler sampler.

INTRODUCTION

It has recently been demonstrated that relatively low concentrations
of formaldehyde (HCHO) in air have potential adverse public health
effects (Gunby 1980, Swenberg et al. 1980). In addition, it has been
shown that significant chronic exposures to HCHO can occur in residen-
tial indoor environments (NRC 1981). The perceived need to protect
residential indoor air quality by maintaining low concentrations of HCHO
and other air pollutants can conflict with energy conservation goals.
The controversy over the use of urea-formaldehyde foam insulation was an
example of this conflict until the use of the material was banned by the
U.S. Consumer Product Safety Commission (Chemistry and Engineering News
1982). Other sources of HCHO are more prevalent in the residential
environment since HCHO is used in many construction materials and con-
sumer goods and is a combustion product. Consequently, residential
weatherization programs, which achieve energy conservation by reducing
building air exchange rates, have the potential to result in deleterious
increases in concentrations of HCHO and other indoor-generated air pol-
lutants. At present, data on HCHO in the residential environment, which
are needed to evaluate this issue, are severely limited.

Investigations of the magnitude and extent of the potential HCHO
problem in the residential environment have been inhibited, in part, by
the lack of simple and inexpensive methods to accurately determine low
concentrations of HCHO in air. In response to this need, several diffu-
sion sampling devices, originally developed for industrial hygiene
applications, are now being marketed for use in residences (e.g., DU
PONT PRO-TEK, 3M Formaldehyde Monitor). However, the suitability of

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these devices for this new application, where it is desirable to measure relatively low concentrations of HCHO over extended time periods, has not been adequately demonstrated.

Lawrence Berkeley Laboratory (LBL) recently has developed a passive sampling device based on the principle of diffusion specifically for the determination of HCHO in residential indoor air (Geisling et al. 1982a). The device, which is inexpensive and easy to use, is capable of accurately measuring time-weighted average concentrations of HCHO from as low as 0.018 ppm to over 1 ppm for a period of one week. The one week sampling interval is ideally suited for quantification of chronic HCHO exposures since HCHO concentrations vary in response to environmental factors such as temperature, humidity, and ventilation (Moschandreas and Rector 1981) which are influenced by occupant activity cycles, e.g., weekday/weekend changes in activities. Peak concentrations are not obtained; however, passive samplers respond quickly to transients, and peak concentrations are incorporated into the time-weighted average (Martin 1981).

This report presents the results of laboratory validation experiments conducted with the LBL passive sampler for HCHO, as well as the results of a field evaluation in which the performance of the passive sampler was compared to that of a reference pump/bubbler sampler. A description of the passive sampler and the results of the laboratory and field validation experiments are summarized in Table 1.

LABORATORY VALIDATION

Sampler Preparation

Passive samplers are prepared as described by Geisling et al. (1982a) with one modification. Sodium bisulfite impregnated filters are dried under vacuum for approximately 3 hr instead of under a constant stream of dry nitrogen. Sampling efficiency, as determined by sampling rate, is not affected by this change in procedure.

Sampler Deployment

Procedures for the deployment of the passive samplers in residences are simple. The date and time of initiation of sampling and identification data are recorded on the passive sampler labels and on a separate data sheet. The samplers are uncapped and attached with masking tape to a suitable surface out of the reach of children and pets. Samplers are hung with their open ends facing down to exclude dust. If replicate samplers are employed, samplers are spaced approximately 2 cm apart. Samplers are not attached directly to surfaces which are potential HCHO sources. In addition, an attempt is made to space samplers out away from walls so that wall effects (e.g., stratified air layers, temperature differentials) are avoided. At the end of a one-week sampling period, the samplers are tightly capped, and the date and time are recorded. The samplers are promptly returned to the laboratory for HCHO analysis.

Analytical Method

The passive samplers are eluted with 6 ml of distilled water upon arrival in the laboratory. If the samplers are not to be analyzed immediately, they are stored in their eluted state in a refrigerator at 5 °C.

Samplers are analyzed for HCHO by the spectrophotometric chromotropic acid (CA) procedure described in P&CAM No. 125 (NIOSH 1977). Specific details of the entire analytical procedure used for the samplers are presented by Geisling et al. (1982a).

Sampling Rate

The sampling rate for diffusion passive samplers is equal to the diffusion coefficient of the contaminant gas in air multiplied by the cross sectional area of the sampler divided by the diffusion path length. Mass uptake is the product of the sampling rate, the ambient concentration, and the sampling time. Sampling rate and the general theory of passive samplers are discussed in detail by Palmes et al. (1976) and Lautenberger et al. (1981).

Since the diffusion coefficient of HCHO in air has not been quantified, it was necessary to empirically determine the sampling rate in the laboratory by exposing the passive samplers to known HCHO concentrations. Test atmospheres at approximately 1 atm and 20 °C were produced with a HCHO gas generation/dilution system (Geisling et al. 1982b). With this system, the production of HCHO gas of known concentrations is achieved by catalytical decomposition of trioxane vapor emanating from a diffusion cell and subsequent dilution with clean air. A calibration

curve was constructed relating the mass of HCHO collected by the samplers to the HCHO exposure (the product of concentration and exposure time) from which the empirical sampling rate was calculated (Geisling et al. 1982a).

In initial tests, the sampling rate for a one-week (168-hr) sampling period was determined to be 3.95 cm^3/min with a standard deviation of 0.17 cm^3/min (Geisling et al. 1982a). Additional laboratory data on the mass of HCHO collected versus HCHO exposure have been collected for one-week periods over a wide range of HCHO concentrations (Table 2). The sampling rate determined from these data by a linear regression weighted for instrumental uncertainties (Bevington 1969) is 4.02 cm^3/min (0.296 µg/ppm-hr) with a standard deviation of 0.11 cm^3/min (Figure 1). The coefficient of determination (r^2) for the regression analysis is 0.996, demonstrating that sampling rate is independent of concentration.

Recent preliminary data indicate that the sampling rate may be moderately higher at sampling periods of less than one week. It is recommended that the passive samplers only be deployed for a period of one week until sufficient data have been collected to accurately quantify the relationship between sampling rate and time.

Detection Limit

The theoretical detection limit of the method is derived from the HCHO concentration that produces an analytical absorbance that is significantly different from the absorbance of the system blank. Passive sampler blanks have a mean absorbance of 0.037 with a standard deviation of 0.005 (Table 3). An absorbance of 0.05 is demonstrated to be signi-

ficantly different from this system blank (p = <0.01) by application of a one-tailed Student's t-test to determine whether a single variate sampled at random could belong to a given population (Sokal and Rohlf 1969). The absorbance of 0.05 is equivalent to a HCHO concentration of 0.07 µg/ml, and the absorbance of the system blank is equivalent to a concentration of 0.02 µg/ml (Figure 2). The difference, 0.05 µg/ml, is attributable to the sample. Since the analytical procedure calls for the elution of the samplers with 6 ml of water, the samplers must collect a minimum of 0.3 µg of HCHO to be at the limit of detection. Use of the 4.0 cm^3/min sampling rate and the recommended deployment period of one week results in a HCHO in air theoretical detection limit of 0.006 ppm.

Field experience with the sampler has shown that precision is often considerably reduced at the theoretical detection limit perhaps due, in part, to the relatively large contribution of the system blank error to the total error at this concentration. Therefore, we recommend the adoption of a lower quantification limit of 0.018 ppm (0.075 absorbance) which is three times the theoretical limit. Precision is considerably improved at 0.018 ppm, and the use of the sampler is not meaningfully restricted since this quantification limit is more than adequate for residential applications.

Upper Quantification Limit

A laboratory experiment demonstrated that the passive sampler has the capacity to collect at least 1500 µg of HCHO from air. However, since the passive sampler is designed specifically for use in residential and office environments, laboratory evaluation of the device has

been limited to a maximum concentration of 1 ppm for 168 hr (50 μg of HCHO collected). ·

Use of the prescribed analytical procedure results in an upper quantification limit of 0.56 ppm. This upper limit, which is established by the maximum linear range of the calibration curve, is sufficient for most residential applications. When the absorbance of the sample exceeds that of the highest aqueous HCHO standard, the upper limit can be extended to well over 1 ppm without loss of the original sample by reduction of the spectrophotometer cuvette path length. The upper limit can also be extended by dilution and reanalysis of the unused portion of the sample. These procedures can produce an upper limit of over 5 ppm for a 168-hr exposure; however, the sampler's linearity of response has not yet been determined for concentrations in excess of 1 ppm.

Precision

Precision was quantified using the coefficient of variation which is simply the standard deviation expressed as a percentage of the mean. The coefficient of variation permits the comparison of the amount of variation in measurements having significantly different means.

The precision of the analytical method alone was determined from routine replicate analyses of aqueous HCHO standards on different days (Table 4). The sample-size-weighted, mean coefficient of variation for the analytical method is 3.2% and is not correlated with HCHO concentration which ranges between zero and 3.9 μg/ml.

The most realistic and useful estimate of the overall precision of the method is obtained from the field comparison (Table 5).

Replicate samplers used in the field comparison were initially clustered in a bundle until it was discovered that deployment of samplers in this manner results in relatively poor precision, perhaps due to starvation of several samplers. Precision was noticeably improved by spacing the samplers approximately 2 cm apart. This spacing is now incorporated into the recommended method of deployment. The six initial field samples with inadequate sampler spacing were excluded from the analysis of precision.

For the 15 field samples employing five or four (an occasional sampler was broken or otherwise lost) replicate samplers spaced 2 cm apart, the coefficient of variation for HCHO concentration ranges between 1.7 and 10.7%. The sample-size-weighted, mean coefficient of variation is 6.7%. The coefficient of variation is not correlated with HCHO concentration which ranges between 0.028 and 0.146 ppm.

Environmental Effects

Since the sampling rate of the passive sampler was established empirically at approximately 1 atm and 20 °C, the mass of HCHO collected by the sampler is standardized at these conditions. From kinetic theory, we know that in real gas diffusion processes the mass of a gas collected is a function of the square root of the absolute temperature and is independent of pressure (Palmes et al. 1976, Lautenberger et al. 1981). The temperature dependence of mass collected is small. For example, an increase in temperature from 20 °C to 25 °C increases the mass collected by only 1%. Therefore, the mass of HCHO collected by the passive sampler can be considered to be independent of both temperature and pressure for most residential applications.

The effect of relative humidity on the collection efficiency of the passive sampler was determined by exposing samplers to a range of relative humidities at 25 °C in a test atmosphere with 0.25 ppm HCHO. Sampling rate was not effected by a one-week exposure at 50-60% relative humidity. However, exposures at 70-85% relative humidity for one week resulted in a significant decrease in sampling rate. Consequently, the passive sampler should not be used in indoor environments where the average relative humidity exceeds 60% at 25 °C.

Interferences

Possible chemical interferences for the CA analytical method are listed in P&CAM No. 125 (NIOSH 1977). Ethanol, phenols, ethylene, propylene, and 2-methyl-1,3-butadiene are reported to produce negative interferences when in excess of HCHO. However, these compounds are normally present in air at lower concentrations than those of HCHO and are not considered to have a serious effect on the method (NIOSH 1977). The possibility that these compounds would interfere in the analysis of the passive samplers is even more remote since they are not expected to be collected by the samplers.

It is possible, however, that acrolein, an unsaturated aldehyde combustion product known to be present in indoor environments primarily as a component of cigarette smoke, could be collected. To test for the potential interference of acrolein with the CA analytical method, passive samplers were spiked with known volumes of aqueous HCHO and acrolein standard solutions. No significant difference in the amount of HCHO was observed between samplers with and without acrolein spikes when acrolein was in an approximate 10:1 excess of HCHO. Since acrolein

concentrations are unli.. y to exceed HCHO concentration. in residential environments (NRC 1981), acrolein is not considered to be an interference.

Storage Stability

Pre-exposure storage stability (shelf life) of the passive samplers has been reported by Geisling et al. (1982a). Samplers were assembled, flushed with nitrogen, capped, and stored for one and two weeks. After storage, they were exposed to approximately 1.4 ppm HCHO in the laboratory test chamber along with freshly prepared samplers. No significant differences were detected with a Student's t-test (p = 0.05) between HCHO concentrations of st⌐red and freshly prepared samplers (Table 6).

Post-exposure storage stability of the passive samplers was also reported by Geisling et al. (1982a). Samplers were exposed to approximately 1.4 ppm HCHO in the laboratory. Concentrations of HCHO determined from samples stored for one and two weeks before analysis were compared to concentrations determined from samples analyzed immediately after exposure. No significant differences were detected with a Student's t-test (p = 0.05) between stored and immediately analyzed samples (Table 7).

FIELD COMPARISON

A field comparison was conducted in occupied residences and an office to determine the accuracy of the passive sampler method relative to the results obtained with a reference pump/bubbler method. Twenty-one individual sampler comparisons were made over a period of three

in a variety of locations which included new energy-efficient houses, weatherized houses, urea-formaldehyde foam insulated houses, conventional houses, and a prefabricated office. The data from these comparisons are summarized in Table 5.

LBL pump/bubbler samplers, which consist of a vacuum pump, flow controller, and refrigerated bubbler trains (Fanning et al. 1981, Miksch et al. 1981) were modified to collect four replicate samples over a period of one week using individual sampling rates near 0.14 L/min. These devices were installed in residences and an office with the sample tube inlet located 10-20 cm from five passive samplers. Sampling was conducted concurrently with both active and passive devices. Pump/bubbler sampler air flow rates were determined at the beginning and end of each one-week sampling period, and average flow rates were used in the calculation of HCHO concentrations. Initial and final flow rates typically varied less than 10% at a sampling location. Total volumes of air passed through the bubblers were corrected to standard pressure; no temperature corrections were made since the measured variation in indoor temperatures around 25 $^{\circ}$C would only result in an approximate $\pm$ 1% variation in sample volume. The HCHO collection efficiency of the bubblers was assumed to be 95% (NIOSH 1977). Bubbler and passive monitor samples were analyzed concurrently using the CA method.

The results obtained by the two sampling methods were statistically compared using a two-way analysis of variance with replication (Sokal and Rohlf 1969). This test demonstrated that there is a significant difference (p = <0.001) between the sets of concentrations measured by the two methods.

In laboratory comparisons, concentrations of HCHO in air determined from bubbler samples collected for periods up to one week are typically within 2% of theoretical concentrations produced by the HCHO gas generation/dilution system. Consequently, we currently accept the bubbler sampler data as the best estimates of the true HCHO concentrations in indoor air for the field comparison. However, the possibility that the pump/bubbler sampler produces biased field results can not be ruled out and is currently being investigated.

The passive sampler concentrations versus pump/bubbler sampler concentrations from the field comparison are plotted in Figure 3. The relationship between the two variables is quantitatively defined by the use of Bartlett's three-group method for regression (Sokal and Rohlf 1969). This regression technique, rather than the standard linear regression, is appropriate when both variables are subject to measurement error. As can be seen in Figure 2, the fit of the data to the regression line is good. We recommend the use of the equation, $Y = 0.87X$, to convert passive sampler concentrations (X) to bubbler sample concentrations (Y) until the discrepancy between the two methods is resolved. With the conversion, the overall accuracy for the passive sampler method is equal to the true concentration with a 95% confidence interval of ± 14%.

SUMMARY

The LBL passive sampler for determining HCHO concentrations in residential indoor air has been validated in laboratory experiments and in a field comparison conducted in occupied residences and an office. The sampler is designed to measure time-weighted average concentrations of HCHO for a period of one week. The quantification range for the one-week period of 0.018 ppm to over 1 ppm is more than adequate for residential applications. The sampler is currently restricted to use in indoor environments where the average relative humidity is 60% or less. Acrolein, the only compound considered to be a significant potential interference, has no effect on the analytical method even when in a 10:1 excess of HCHO. Product shelf life and post-exposure sample stability of two weeks minimum are sufficient for residential survey applications. The overall precision obtainable with the sampler in the field is approximately 7%. When a correction factor is applied to compensate for presumed bias, the overall accuracy of the method in the field is equal to the true concentration plus and minus a 95% confidence interval of 14%.

The passive sampler is now developed and tested to a stage where it can be used with confidence to determine HCHO concentrations in residences; however, method validation efforts are continuing. The relationship between sampling rate and time for sampling periods shorter than one week is being characterized. The effect of high relative humidity on the performance of the sampler is being defined more rigorously. Finally, the source of the discrepancy between results obtained with the passive sampler and the pump/bubbler sampler is under investigation.

ACKNOWLEDGMENT

REFERENCES

Bevington, P.R., 1969, <u>Data</u> <u>Reduction</u> <u>and</u> <u>Error</u> <u>Analysis</u> <u>for</u> <u>the</u> <u>Physi-cal</u> <u>Sciences</u>, McGraw-Hill, Inc., New York, NY.

Chemistry and Engineering News, March 29, 1982, "Effects of foam insulation ban far reaching," pp. 34-37.

Fanning, L.Z., J.R. Allen, and R.R. Miksch, 1981, "Instructions for operating LBL formaldehyde sampler," Lawrence Berkeley Laboratory report LBL-10629, Berkeley, CA.

Geisling, K.L., M.K. Tashima, J.R. Girman, R.R. Miksch, and S.M. Rappaport, 1982a, "A passive sampling device for determining formaldehyde in indoor air," Lawrence Berkeley Laboratory report LBL-12560 revised, Berkeley, CA.

Geisling, K.L., R.R. Miksch, and S.M. Rappaport, 1982b, "Generation of dry formaldehyde at trace levels by the vapor-phase decomposition of trioxane," <u>Anal</u>. <u>Chem</u>. <u>54</u>:140-142.

Gunby, P., 1980, "Fact or fiction about formaldehyde," <u>J</u>. <u>Am</u>. <u>Med</u>. <u>Assoc</u>. <u>243</u>:1697-1703.

Lautenberger, W.J., E.V. Kring, and J.A. Morello, 1981, "Theory of passive monitors," W.D. Kelley, ed., <u>Annals</u> <u>of</u> <u>the</u> <u>American</u> <u>Conference</u> <u>of</u> <u>Governmental</u> <u>Industrial</u> <u>Hygienists</u> - <u>Dosimetry</u> <u>for</u> <u>Chemical</u> <u>and</u> <u>Physical</u> <u>Agents</u>, American Conference of Governmental Industrial Hygienists, Cincinnati, OH, pp. 91-99.

Martin, J.E., 1981, "An intuitive approach to passive monitors," W.D. Kelley, ed., Annals of the American Conference of Governmental Industrial Hygienists - Dosimetry for Chemical and Physical Agents, American Conference of Governmental Industrial Hygienists, Cincinnati, OH, pp. 101-106.

Miksch, R.R., D.W. Anthon, L.Z. Fanning, C.D. Hollowell, K. Revzan, and J. Glanville, 1981, "Modified pararosaniline method for the determination of formaldehyde in air," Anal. Chem. 53:2118-2123.

Moschandreas, D.J. and H.E. Rector, 1981, "Radon and aldehyde concentrations in the indoor environment," Lawrence Berkeley Laboratory report LBL-12590, Berkeley, CA.

National Institute of Occupational Safety and Health, 1977, NIOSH Manual of Analytical Methods, 2nd ed., Publication No. 77-157A, National Institute of Occupational Safety and Health, Cincinnati, OH.

National Research Council, 1981, Indoor Pollutants, National Academy Press, Washington, D.C.

Palmes, E.D., A.F. Gunnison, J. DiMattio, and C. Tomczyk, 1976, "Personal sampler for nitrogen dioxide," Am. Ind. Hyg. Assoc. J. 37:570-577.

Sokal, R.R. and F.J. Rohlf, 1969, Biometry, W.H. Freeman and Company, San Francisco, CA.

Swenberg, J.A., W.D. Kerns, R.I. Mitchell, E.J. Gralla, and K.L. Parkov, 1980, "Induction of squamous cell carcinomas of the rat nasal cavity by inhalation exposure to formaldehyde vapor," Cancer Res. 40:3398-3402.

Table 1. Description and specifications of the LBL passive sampler.

CONTAMINANT: Formaldehyde (HCHO)

SAMPLER: Passive diffusion sampler; area, 3.98 cm^2; path
                      length, 9.4 cm; collection medium, NaHSO$_3$
                      impregnated glass fiber filter

ANALYSIS: Chromotropic acid spectrophotometric
                      analysis, NIOSH P&CAM No. 125

SAMPLING RATE: 4.02 cm^3/min (0.296 μg/ppm-hr) at 1 atm and 20 °C

SAMPLING PERIOD: 1 week (168 hr)

                      0.018
SAMPLING RANGE: ~~0.18~~ ppm to more than 1 ppm for 168 hr

ENVIRONMENTAL   Independent of pressure, only slightly
EFFECTS: dependent on temperature

                      Accuracy reduced when average relative
                      humidity exceeds 60% at 25 °C

INTERFERENCES: No identified significant interferences
                      in residential environments

SHELF LIFE: 2 weeks minimum

SAMPLE STABILITY: 2 weeks minimum

OVERALL PRECISION: Mean coefficient of variation = 6.7%

BIAS: +15% based on field comparisons with
                      reference method; true concentration =
                      0.87 x passive sampler concentration

OVERALL ACCURACY: True concentration ± 95% confidence
                      interval of 14%

Table 2. Mass of HCHO collected by passive samplers versus HCHO exposure.

HCHO Exposure Conc. (ppm)	Exposure Time (hr)	Exposure (ppm-hr)	n*	Mass of HCHO Collected (μg) x ± s.d.†
0.058	163	9.45	10	2.96 ± 0.218
0.096	154	14.8	10	4.39 ± 0.173
0.201	141	28.3	9	8.40 ± 0.265
0.211	169	35.7	10	9.59 ± 1.04
0.397	159	63.1	10	17.5 ± 1.75
0.839	160	134	9	39.4 ± 2.40
1.00	165	165	10	49.2 ± 1.79
1.00	166	166	12	55.5 ± 3.42

*Number of samplers.

†s.d. = standard deviation.

Table 3. Absorbances of passive sampler blanks.

Date Analyzed	Lot. No.	Absorbance
3-31	A	0.034
		0.038
4-14	B	0.045
		0.029
		0.047
4-21	C	0.040
		0.041
		0.039
4-26	D	0.036
		0.035
		0.037
5-3	E	0.042
		0.023
		0.036
5-17	F	0.033
		0.030
		0.037
5-17	II	0.038
		0.032
		0.036
5-19	G	0.035
		0.039
		0.040
	$\bar{x}$ =	0.037
	s.d. =	0.005
	CV[*] =	13.5%

[*]Coefficient of variation.

Table 4. Precision of analytical method as measured by the coefficient
of variation. Routine analysis on different days.

HCHO Concentration (μg/ml)	n	Coefficient of Variation (%)
0	6	4.2
0.194	6	5.6
0.388	6	3.1
0.766	7	3.1
1.55	8	3.1
1.94	7	1.5
2.32	7	1.8
3.10	5	1.3
3.88	6	3.0

Weighted mean = 3.2

Table 5. Field comparison of the performances of the LBL passive sampler and a reference pump/bubbler sampler.

	Bubbler	Passive	Bubbler	Passive	Bubbler	Passive
Location	S-6		S-10		S-15	
n	4	4	4	5	4	5
x (ppm)	.127	.146	.100	.107	.117	.140
± 95% c.l.	.035	.014	.019	.002	.053	.009
s.d. (ppm)	.022	.009	.012	.002	.033	.007
CV (%)	17.3	6.2	12.0	1.9	28.2	5.0
Location	S-16		S-17		CS-11	
n	4	4	4	5	4	4
x (ppm)	.102	.124	.098	.105	.065	.060
± 95% c.l.	.022	.018	.024	.004	.003	.024
s.d. (ppm)	.014	.011	.015	.003	.002	.015
CV (%)	13.7	8.9	15.3	2.8	3.1	25.0[*]
Location	CS-13		CS-14		CS-17	
n	4	5	4	5	4	5
x (ppm)	.063	.081	.074	.087	.065	.069
± 95% c.l.	.019	.020	.006	.011	.010	.024
s.d. (ppm)	.012	.016	.004	.009	.006	.019
CV (%)	19.0	19.8[*]	5.4	10.3[*]	9.2	27.5[*]
Location	CS-20		CS-23		CS-31	
n	4	4	4	5	4	5
x (ppm)	.026	.031	.042	.053	.033	.042
± 95% c.l.	.003	.011	.022	.005	.005	.004
s.d. (ppm)	.002	.007	.014	.004	.003	.003
CV (%)	7.7	22.6[*]	33.3	7.5	9.1	7.1

[*]Excluded from analysis of precision - see text, page 8.

Table 5. Field comparison of the performances of the LBL passive sampler and a reference pump/bubbler sampler. (cont.)

	Bubbler	Passive	Bubbler	Passive	Bubbler	Passive
Location	CS-34		CS-44		CS-49	
n	4	5	3	3	4	5
x (ppm)	.046	.042	.100	.117	.034	.043
± 95% c.l.	.002	.007	.027	.007	.002	.004
s.d. (ppm)	.001	.006	.011	.003	.002	.003
CV (%)	2.2	14.3*	11.0	2.6	5.9	7.0
Location	CS-62		O-2		44B-1	
n	4	5	4	5	4	5
x (ppm)	.026	.028	.072	.082	.049	.056
± 95% c.l.	.008	.002	.019	.006	.006	.007
s.d. (ppm)	.005	.002	.012	.005	.004	.006
CV (%)	19.2	7.1	16.7	6.1	8.2	10.7
Location	44B-2		44B-3		44B-4	
n	4	5	4	4	4	5
x (ppm)	.046	.052	.051	.060	.052	.055
± 95% c.l.	.006	.002	.010	.002	.010	.004
s.d. (ppm)	.004	.002	.006	.001	.006	.003
CV (%)	8.7	3.8	11.8	1.7	11.5	5.5

*Excluded from analysis of precision – see text, page 8.

Table 6. Pre-exposure storage stability (shelf life) of passive samplers.

| Storage Time (wk) | HCHO Concentration (ppm) | | Ratio Stored/Non-stored |
	Stored Prior to Exposure* $x \pm$ s.d.	Exposed Immediately after Preparation+ $x \pm$ s.d.	
1	1.42 ± 0.07 (n=7)	1.40 ± 0.05 (n=4)	1.01
2	1.36 ± 0.01 (n=8)	1.33 ± 0.07 (n=4)	1.02

*Passive samplers were prepared, flushed with N_2, capped, and stored at room temperature before exposure to HCHO.

+Stored and non-stored samplers were exposed to the same test atmosphere.

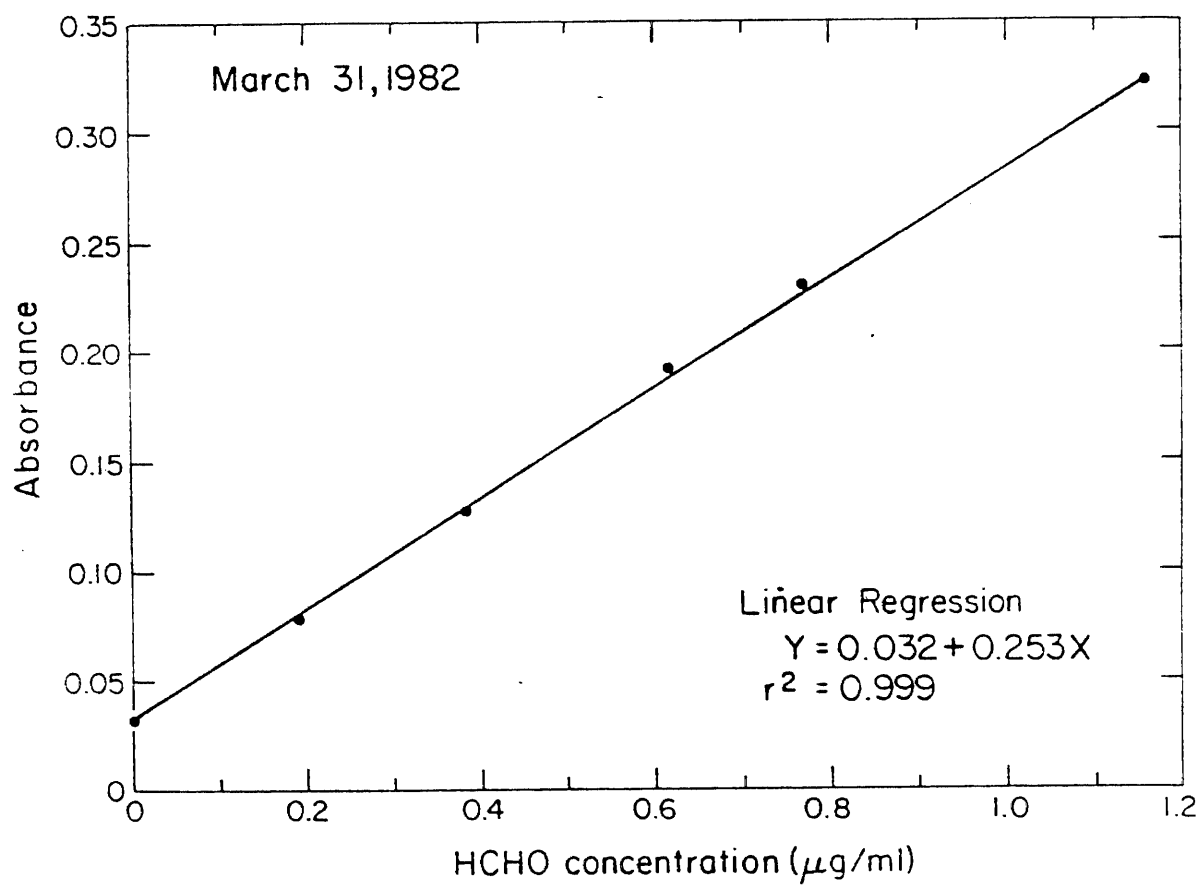Table 7. Post-exposure storage stability of passive samplers.

| Storage Time (wk) | HCHO Concentration (ppm) | | Ratio Stored/Non-stored |
	Stored after Exposure* $x \pm$ s.d.	Analyzed Immediately after Exposure $x \pm$ s.d.	
1	1.24 ± 0.07 (n=7)	1.35 ± 0.09 (n=5)	0.92
2	1.41 ± 0.06 (n=8)	1.36 ± 0.02 (n=4)	1.04

*Passive samplers were stored at room temperature.

Linear regression
$$Y = 0.033 + 0.296X$$
$$r^2 = 0.996$$
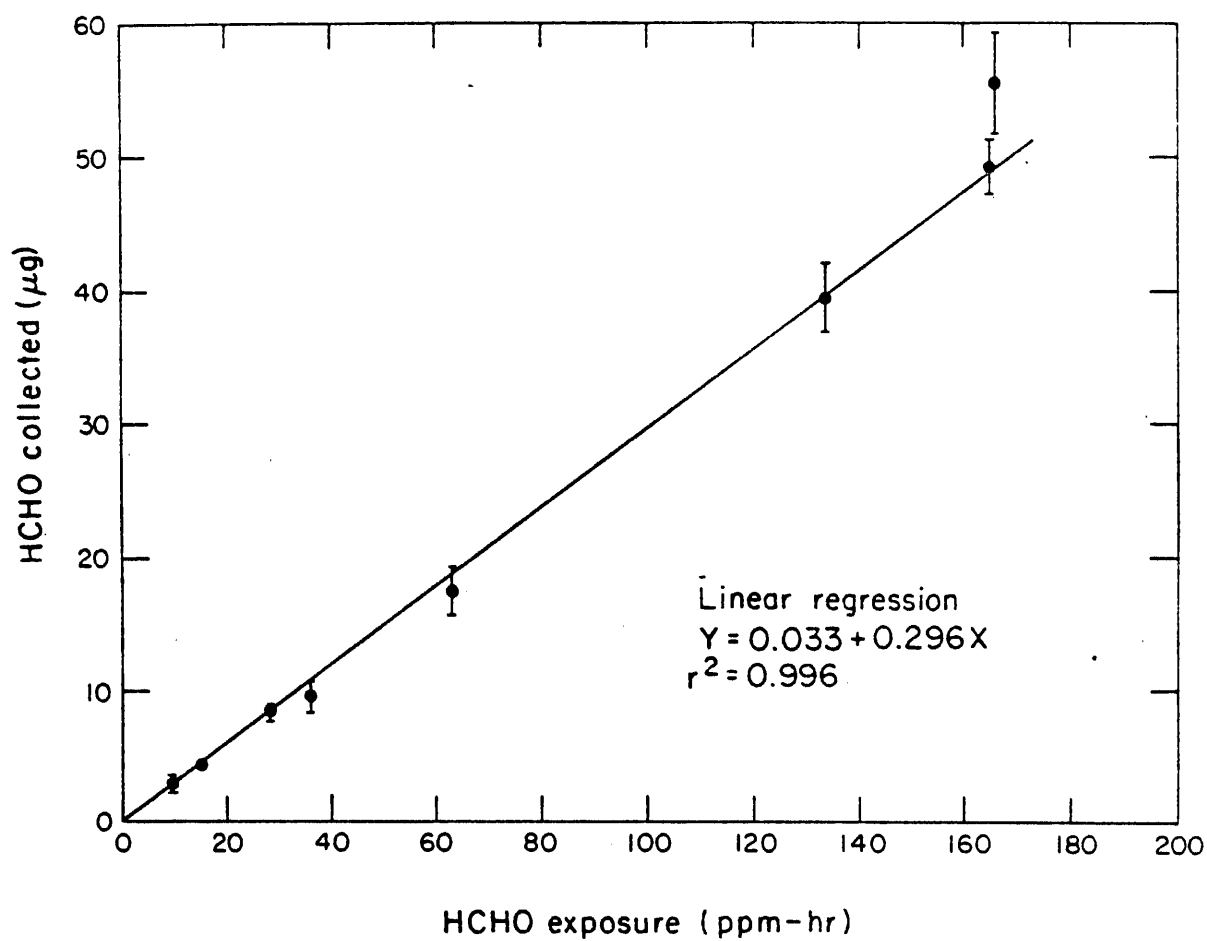
Figure 1   Mass of HCHO collected by the passive   sampler   versus   HCHO
exposure.   Data are from Table 2.

March 31, 1982

Linear Regression
$$Y = 0.032 + 0.253X$$
$$r^2 = 0.999$$

Absorbance

HCHO concentration (μg/ml)

XBL 826-323

Figure 2   Calibration curve for chromotropic acid method of HCHO analysis.   Absorbance versus concentration of aqueous standards.
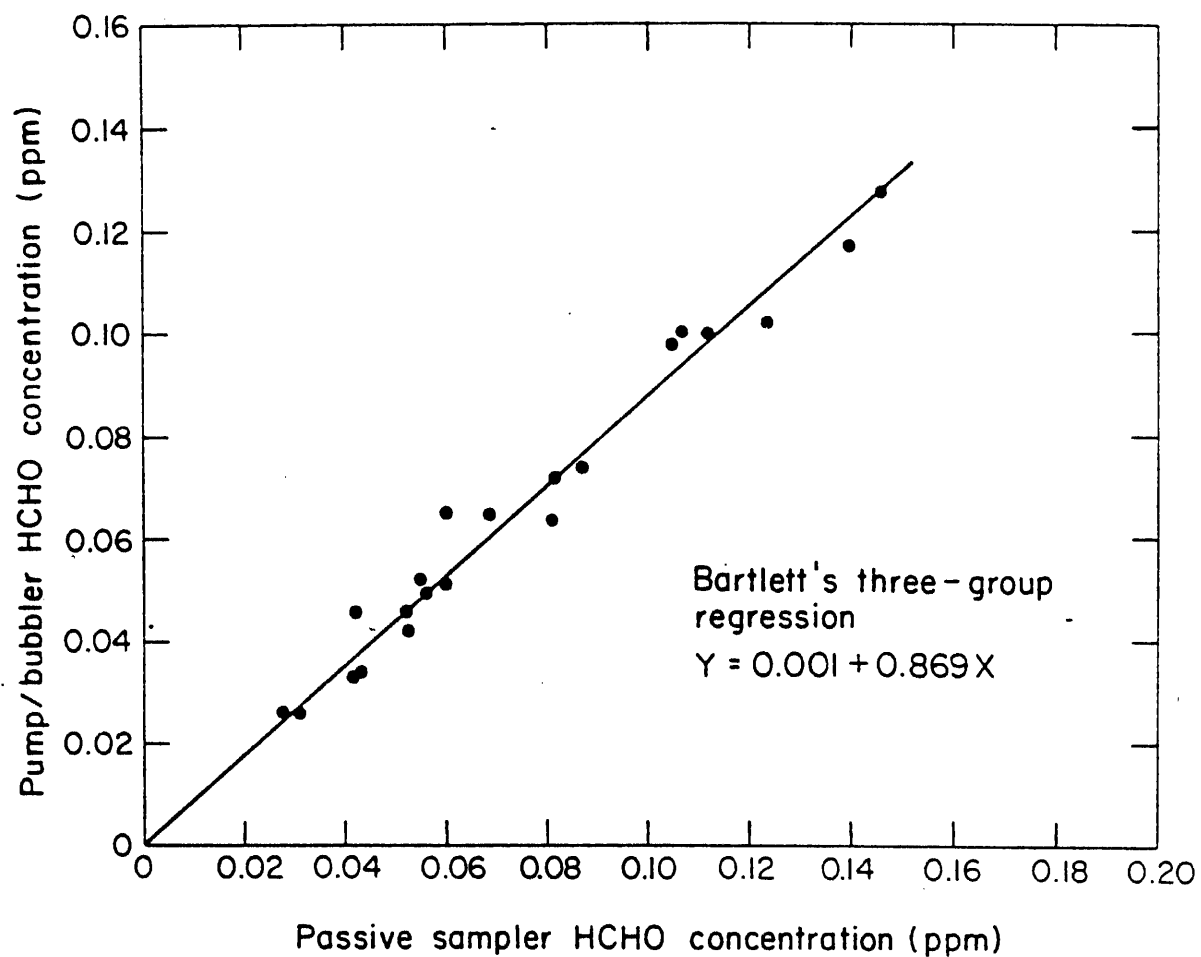
Figure 3   Passive sampler HCHO concentrations versus pump/bubbler sampler concentrations for 21 field comparisons.

APPENDIX D

RESULTS OF QUALITY ASSURANCE ANALYSIS

D.1   IMPINGER SAMPLES

All impinger samples were analyzed in a "blind" mode, i.e., the only information made available by SAI staff to ERT prior to analysis and data reporting was the sample code number. Ninety-two (92) samples were analyzed for formaldehyde only, and nine (9) samples were analyzed for formaldehyde, acetaldehyde, acetone, acrolein, propanal, n-butanal, methyl ethyl ketone (2-butanone), n-hexanal and benzaldehyde. The samples were received and analyzed in three batches, and each of the three corresponding data reports included results for laboratory reagent blank values for all carbonyls.

Table D.1-1 shows the quality assurance (QA) samples taken by SAI in the field. These samples were limited to formaldehyde, and included three types of studies:

(1) Side-by-side samples to assess reproducibility of the entire sampling and analytical protocol. One sample of this type (labeled "parallel" in Table D.1-1) was collected;

(2) Two impingers in series to assess collection efficiency. Three samples of this type (labeled "series" in Table D.1-1) were collected; and

(3) Field controls, involving transfer of the reagent to the sampling device but no active sampling, in order to estimate the possibility of contamination during field sampling. Five· samples of this type (labeled "blanks" in Table D.1-1) were collected.

Table D.1-1
QUALITY ASSURANCE SAMPLES

Site	Type	SAI Numbers	Formaldehyde	
			µg	ppb
L.A. Intl. Airport	Blank	1-5	0.49[a]	-
	Parallel	1-3, 1-7	1.4, 1.28	19.6, 15.1
Mobil Oil	Series	2-7(F)	1.1	15.1
		2-1(B)	Lost by ERT	
Reichhold	Blank	9-5	0.23[b]	-
Home	Series	7-1(F)	1.77	22.2
		7-2(B)	0.20	2.5
Lennox (January)	Blank	3-5	0	0
Pico-Rivera (January)	Blank	4-9	0.03[c]	-
Pico-Rivera (May)	Series	1-3(F)	0.30	5.2
		1-4(B)	19.56	336.5
	Blank	1-6	0.02[d]	-

[a] Other samples ranged from 0.47 to 2.25 µg.

[b] Other samples ranged from 0.59 to 2.54 µg.

[c] Other samples ranged from 0.26 to 2.72 µg.

[d] Other samples ranged from 0.23 to 0.39 µg, except for the possibly erroneous Sample No. 1-4.

The following observations can be made for each type of QA sample:

D.1.1   Field Controls

In the absence of contamination during sample handling in the field, amounts of formaldehyde in the field control samples should be equivalent to those measured in the corresponding laboratory reagent blanks. More specifically, contamination during field handling will be indicated by field control values exceeding a lowest detection limit (LDL) of 0.20 μg, which is conservatively estimated as three times the standard deviation for laboratory reagent blanks. The results shown in Table D.1-2 indicate that one of the five field controls collected early in the project may have been contaminated during field handling.

D.1.2   Parallel Samples

The average formaldehyde concentration of the one parallel set collected was 17.35 $\pm$ 2.25 ppb. The $\pm$13-percent difference is higher than what is typically obtained at formaldehyde levels of ~15 to 20 ppb, i.e., 5 to 10 percent. However, this set was collected as part of the same batch which included the single field sample contaminated during handling, therefore suggesting that problems in field handling may by reflected, in part, in the marginally acceptable $\pm$13-percent reproducibility. More than one sample of this type should have been collected.

D.1.3   Series Samples

Three series were collected. Unfortunately, they included the only 2 samples lost out of 92 samples analyzed for formaldehyde. Sample #2-1, a back-up impinger, was lost upon addition of a contaminated internal standard. Sample #1-4, another back-up sample, was obviously contaminated with ~20 μg of formaldehyde while the corresponding upstream sample contained only 0.30 μg. The source of the contamination is unknown but may have involved contaminated glassware and/or tube cap. The third set of samples indicated a collection efficiency of ~100 percent since the amount of formaldehyde

Table D.1-2

COMPARISON OF FIELD CONTROL SAMPLES AND REAGENT BLANKS

Sample No.	Formaldehyde µg/Sample	Reagent blank, µg/Sample[a]
1-5	0.49	0.20
9-5	0.23	0.20
3-5	0	0.20
4-9	0.03	0.20
1-6	0.02	0.20

[a] Detection limit = 3σ of reagent blank value, see text.

collected in the back-up (downstream) impinger was identical to the detection limit. This result is in agreement with those of numerous collection efficiency studies ERT has conducted in the past. More samples of this type could have been collected to compensate for the two contaminated samples.

D.2   PASSIVE MEASUREMENT SAMPLES

The passive formaldehyde samplers used for the indoor air sampling were also analyzed blind; Lawrence Berkeley Laboratory was provided only with code numbers. As was reported in Section 5.2.5, pairs of samplers were colocated in six residences. Five complete pairs were returned to SAI for analysis. Table D.2-1 shows the results of the quality assurance analysis. The absolute difference between the two values ranged from 1.6 to 26.1 percent of the mean. The average absolute difference between pairs was 3.8 ppb.

Table D.2-1
RESULTS OF ANALYSES OF COLOCATED PASSIVE FORMALDEHYDE
SAMPLER PAIRS
(Concentrations in ppb)

Sample No.	Sampler 1	Sampler 2	Absolute Difference	Pct. Difference
1	32	33	1	3.2
2	36	30	6	18.2
3	64	63	1	1.6
4	39	34	5	13.7
5	20	26	6	26.1

APPENDIX E

INDOOR AIR SAMPLING SURVEY FORMS

FORMALDEHYDE·SAMPLE SITE SELECTION FORM

RANDOM SAMPLE NO. _____

NAME _____

STREET _____

CITY/STATE/ZIP _____

PHONE _____

Phone Contact and Screening Information

Date/Time

Subject Contacted

No Answer

Other

      [] Meets criteria
        [] Agrees
        [] Refuses

      [] Doesn't meet criteria

RESIDENCE:

[] Owner [] Renter
[] Single Unit [] Other:_____
[] Urban [] Rural
[] No. Coast [] S.F. Bay Area [] Sacramento Valley [] San Joaquin Valley
[] L.A. - Long Beach

Age of Housing:

[] 33+
[] 21-32
[] 11-20
[] New - 10
[] New, Energy efficient

WORK:

Type of Building: _____

Window: [] Closed [] Able to open

Carpeting? [] Yes [] No

Underground Parking [] Yes [] No

Able and willing to sample at work? [] Yes [] No

Sampling Information

Sample # _____ Lot # _____ [] Residence [] Work

Sample # _____ Lot # _____ [] Residence [] Work

Date sampler(s) mailed _____

Date/time sampling began _____

Date/time sampling ended _____

Date sampler and forms received at SAI _____

Date gift certificate mailed _____

AIR RESOURCES BOARD

1102 Q STREET
P.O. BOX 2815
SACRAMENTO, CA 95812

(916) 445-0753

November 22, 1982

This letter is to confirm that Science Applications, Inc. (SAI) is under contract to the Air Resources Board (ARB) to conduct a statewide inventory of formaldehyde sources and concentrations. This contract, entitled "Formaldehyde: A Survey of Airborne Concentrations and Sources" (Contract No. A2-059-32) requires the contractor to survey producers and users of formaldehyde and formaldehyde-containing compounds, collect emissions data, and to measure formaldehyde concentrations in residences, workplaces and in ambient air.

Science Applications, Inc. is required to preserve in strict confidence all information designated "trade secret" which is obtained from business entities during performance of this contract and may not retain, disclose or in any other manner use such information except to report it to duly authorized members of the Air Resources Board staff. The ARB will maintain the confidentiality of trade secret data in strict accordance with State and federal law.

The Air Resources Board would appreciate your firm's cooperation with SAI in the performance of this contract. Thank you for your assistance.

Sincerely yours,

John R. Holmes, Ph.D.
Chief, Research Division

Figure 5.1-4   ARB Formaldehyde Study Authorization Letter

Hello. My name is _____. I'm a scientist with a company called Science Applications. The State of California has asked us to measure formaldehyde levels in a sample of homes throughout California. Your home was chosen at random. I'm hoping you will be kind enough to help us - no one will come out to your home; it will only take 15 to 30 minutes of your time; and we'll give you a $5 gift certificate to Safeway or McDonald's for your trouble.

Let me briefly tell you about the survey and then you can tell me if you would like to participate.

The purpose of this survey is to measure the amount of indoor formaldehyde at various homes and workplaces in California. What we will ask you to do is very simple. We will send you a letter explaining the survey and giving instructions on exactly what to do. We will also send a small glass tube and two short checklists. The small glass tube is a formaldehyde sampler; it measures the amount of formaldehyde in the air - you simply uncap the tube, record the date/time the cap was removed, and tape it to a wall or door at nose level. One week later, replace the cap, and record the date/time the cap was replaced. We will also ask you to fill out 2 short checklists - one asks 4 questions about your home; the other asks 5 questions about events in your home during the week the glass tube was uncapped. You will mail the tube and checklists back to us. Then we will mail you your 5$ gift certificate. There's not much to it - we estimate it will take 15-30 minutes of your time.

Would you like to participate?

IF NO: Thank you for your time. Goodbye.

<u>IF YES:</u>

I need to ask you 4 questions about your home to see if it qualifies for our survey:

      1. Do you live in a house, or another type of building (e.g., apartment, condominium, mobile home, townhouse, duplex, etc)?

      2. Do you own or rent?

      3. Would you say the area you live in is urban or rural?

      4. How old is the building you live in?

        <u>If new</u>: is it an "energy-efficient" building (e.g., cracks sealed to reduce air flow)?

<u>IF DOES NOT MEET CRITERIA:</u>

I'm sorry, your home doesn't have the characteristics we are looking for - we can't use your home in our survey. Thank you for your time, though. Goodbye.

<u>IF DOES MEET CRITERIA</u>

      <u>If selecting work site:</u>

I would like to ask you 5 questions about you workplace:

1. Do you spend most of your work-day indoors, or outdoors?

2. What type of building do you work in?

3. Is you workplace carpeted?

4. Does your building have underground parking?

5. Are the windows at your workplace permanently closed, or can they be opened?

Your home [and workplace] meet[s] the requirements for our survey.

        If also selecting work site:

        Would you also be willing to place a sample at your workplace?

Which $5 gift certificate would you like:
Safeway or McDonalds?

Let's verify your address: [verify address]

Thank you for your time and cooperation. We'll be sending the materials to
you in a few days. Goodbye.

INDOOR FORMALDEHYDE
COVER LETTER: 1 HOME SAMPLE

[Date]

[Name]
[Address]
[City/State/Zip]

Dear [Name]:

A scientist from our office recently talked with you on the telephone. As was explained, we are under contract to the California Air Resources Board to survey the amount of formaldehyde present in the indoor air of homes and workplaces throughout California. Your home was one of 80 homes randomly chosen for formaldehyde measurement. The survey will·take 15 to 30 minutes of your time, for which we will send you a $5 gift certificate to Safeway or McDonalds. Thank you for agreeing to help with this important survey.

Enclosed you will find the folllowing items:

      o Formaldehyde sampler (small glass tube), with a small piece of styrofoam and adhesive tape

      o Instructions for the use of the sampler

      o Checklist asking questions about your home

      o Checklist asking questions about events which occur in your home during the period of sampling

      o Return envelope

The tasks we would like you to do are summarized below:

1. Place the formaldehyde sampler in your home for 1 week. ·Please refer to the "Instructions For Use of Sampler" for exact instructions.

2. Fill out the "Sample Site Data Sheet" (4 questions)

3. At the end of sampling, fill out the "Sampling Week Data Sheet" (5 questions)

4. Return sampler and the two data sheets to our office, using the enclosed return envelope. Your gift certificate will be promptly mailed to you after the items are returned to us.

The tasks we are asking you to complete are simple. However, if you have any questions about the tasks, or about the survey in general, do not hesitate to call our office, collect, at (213) 553-2705. Ms. Karen Shishino or I will answer any questions you may have.

INSTRUCTIONS FOR USE OF SAMPLER

The procedures for the use of the sampler are simple. The following is a step-by-step list of instructions. Please follow these instructions exactly, and in order. Please read through all instructions before beginning.

1. SELECT SITE IN YOUR HOME FOR PLACEMENT OF SAMPLER

    a. Pick a room in your home that your family frequently occupies. For example, you might select the room the T.V. is in. The living room would be a good choice. However, DO NOT place the sampler in the kitchen or bathroom.

    b. After selecting a room, select the exact spot to place the sampler. The sampler is to be taped to a wall or door at "nose level," approximately 5 feet above the floor. DO NOT place the sampler next to an open window. Select a spot at which the tape will not damage the paint finish of the wall. Also, select a spot where the sampler is not likely to be accidently knocked off.

    c. Record the location of the sampler on the "Sample Site Data Sheet" at "I.A. Location of Sampler."

2. BEGIN SAMPLING

    Sampling is begun by the following steps:

    a. Two pieces of tape, to be used to attach the sampler to the wall or door, are provided for your convenience. These pieces of tape are wrapped around the glass sampler. Remove these two pieces of tape, now, and store them in a convenient spot. These pieces of tape will be used in the steps below.

    b. Remove the red tape wrapped around one end of the sampler (save-don't discard!).

    c. Remove the red cap from the end of the sampler. Don't discard this cap - it will be used to re-cap the sampler at the end of the sampling period. Store the red cap on the opposite (closed) end of the sampler.

    d. Wrap the red tape around the red cap. The red tape will be used to seal the sampler at the end of sampling.

    e. There is a white label wrapped around the sampler. On this label write the date and time the sampler was uncapped. Also write this information on the "Sample Site Data Sheet" at "I.A. Date/Time Sampler Uncapped."

    f. ATTACH SAMPLER TO WALL

        The sampler is to be taped to the wall, separated from the wall by the 2 enclosed pieces of styrofoam, with the open end of the

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sampler facing down (we don't want to collect dust). One piece of styrofoam is to be placed near the top of the sampler, and the other is to be placed near the bottom, as shown in figures 1 and 2. Place the pieces of styrofoam next to the wall (or door) at nose level. Place the sampler on the styrofoam, open end facing down. Place the adhesive tape around the sampler, attaching the sampler and styrofoam to the wall (or door).

g. The sampler should now be attached to the wall (or door) as pictured in figures 1 and 2.

3. END SAMPLING

The sampler is to remain attached to the wall (or door) for <u>1 week</u>.

a. At the end of 1 week remove the sampler from the wall.

b. Remove the red tape and red cap from the closed end of the sampler.

c. Place cap over the open end of the sampler, closing the sampler, and wrap the red tape around cap and sampler to seal tightly.

d. Record the date and time the cap was replaced on the "Sample Site Data Sheet" and also on the white sampler label.

SAMPLE SITE DATA SHEET

I. Sampling information
    A.   Residence sample no. _____

           Date/time sampler uncapped _____
           Date/time sampler re-capped _____
           Location of Sampler _____

    B.   Workplace sample No. _____

           Date/time sampler uncapped _____
           Date/time sampler re-capped _____
           Location of Sampler _____

II. Please place an "X" beside the following characteristics that describe your residence.

    A.   Which of the following is the <u>primary</u> heating source in your home? (Please choose one)

           [] Central heating, gas
           [] Central heating, electric
           [] Individual room heater, gas
           [] Individual room heater, electric
           [] Kerosene heater
           [] Other. Please describe: _____

    B.   Which of the following methods do you usually use in your home for cooking food? (Please choose one)

           [] Utility gas
           [] Electricity
           [] Other. Please describe: _____

    C.   Which of the following describes your home? (choose any that apply; you may choose more than one)

           [] Insulation (wall or attic)
           [] Urea-formaldehyde foam insulation (sprayed-in foam insulation)
           [] Recent renovation of the kitchen, including the installation of new cabinets
           [] Large area in home recently recarpeted (within the last year)
           [] Energy-Efficient home (e.g., cracks sealed to reduce air flow)

    D.   How many rooms in your residence (excluding bathrooms)? _____

III. Remarks. Record any comments or unusual circumstances below.

_____

_____

_____

SAMPLING WEEK DATA SHEET

Check any of the following which occurred in your home during the week the sampler was uncapped.

1. Did you heat your home during this week?

   [] No
   [] Yes. How would you describe you use of heating equipment?

      [] low use
      [] moderate use
      [] high use

2. Did you cook any meals during this week?

   [] No
   [] Yes. Number of meals cooked _____

3. Were your windows open at any time during this week?

   [] No
   [] Yes

4. Did you use a fireplace during this week?

   [] No
   [] Yes. What type of fuel was burned?
   [] Natural gas
   [] Wood
   [] Other. Please describe: _____

5. Were any cigarettes smoked in your home during the week of sampling?

   [] No
   [] Yes. How would you describe the number of cigarettes smoked in your home during this week?

      [] low (1 pack or less)
      [] medium (more than 1 pack, less than 5 packs)
      [] high (more than 5 packs)

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